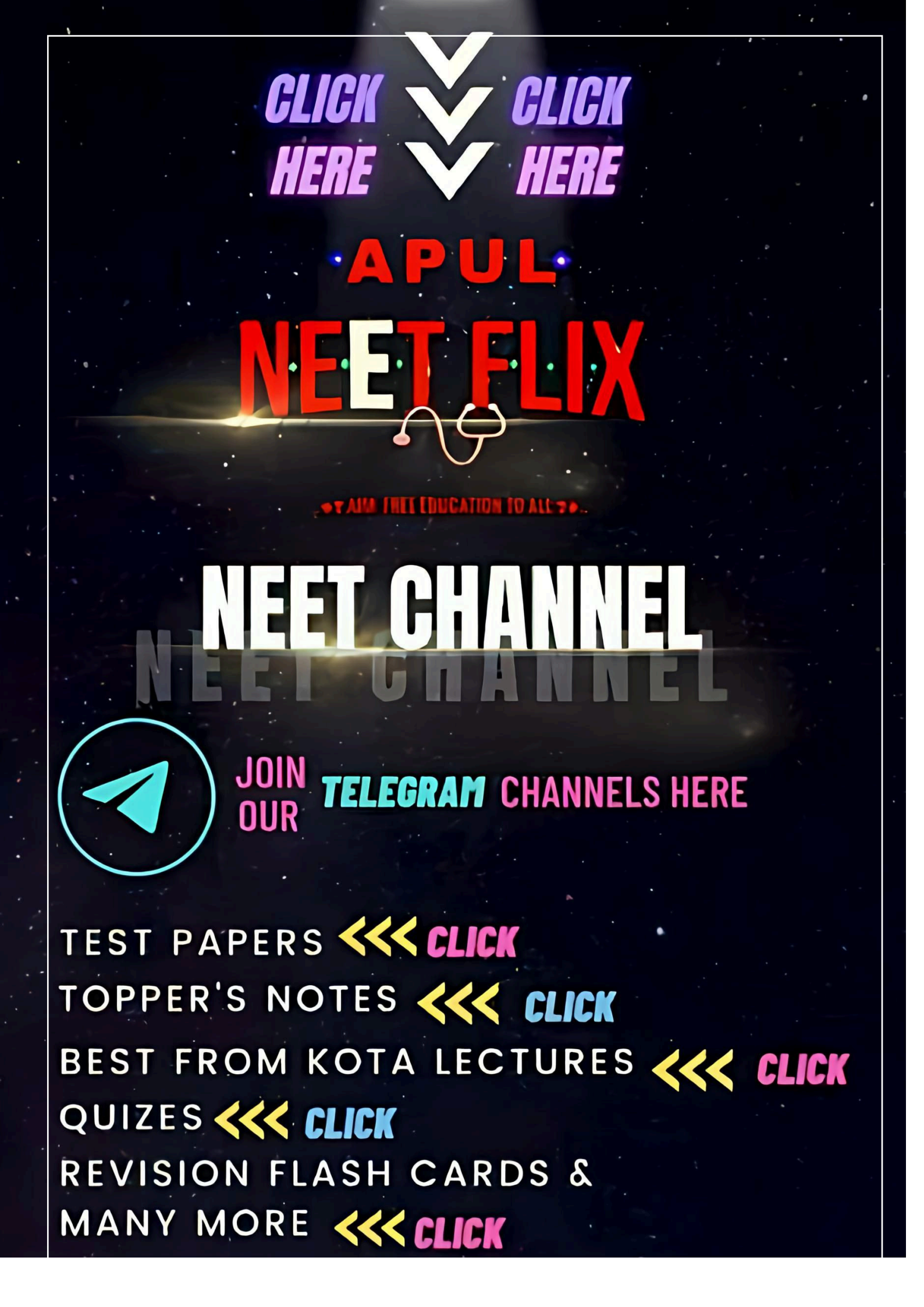
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HANDBOOK OF CHEMISTRY FOR NEET-UG

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PREFACE

Welcome to the exciting world of competitive exams, where success is determined by your preparation and dedication. At ALLEN Career Institute, we believe in providing you with the best tools and resources to help you achieve your goals.

Our Chemistry Handbook has been exclusively designed by experienced faculties to help NEET (UG) aspirants revise all the important concepts in a concise and diagrammatic manner. It's an indispensable tool for memorizing and revising each and every concept of chemistry in a very short time.

Prepared by a pool of expert faculties, this handbook helps you to compete with the best brains in the NEET (UG) exam. Its pictorial and flow chart representation of concepts are more impressive as tools for understanding and reasoning, ensuring effective time management during exams. It helps to test your knowledge and provide a comprehensive revision of the subject.

Using ALLEN's Chemistry Handbook for last-minute revision for NEET (UG) is the best way to boost your confidence level and ensure that you are well-prepared for the exam. So, get ready to ace your NEET (UG) exam with the help of ALLEN's Chemistry Handbook, your trusted partner in the journey to excellence!

Best Wishes

Expert Faculty Team

ALLEN

HANDBOOK OF CHEMISTRY

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PHYSICAL CHEMISTRY

CHAPTER 01

SOME BASIC CONCEPTS OF CHEMISTRY

SOME USEFUL CONVERSION FACTORS

1 Å = 10^{-10} m, 1 nm = 10^{-9} m

1 pm = 10^{-12} m

1 L = 10^{-3} m^3 = 1 dm^3

1 atm=760 mm Hg or torr=101325 Pa or Nm^{-2}

1 bar = 10^5 Nm^{-2} = 10^5 Pa

1 calorie = 4.184 J

1 electron volt (eV) = 1.6022×10^{-19} J

(1 J = 10^7 ergs)

(1 cal > 1 J > 1 erg > 1 eV)

ATOMIC MASS OR MOLECULAR MASS

Mass of one atom or molecule in a.m.u.

C → 12 amu

H_2O → 18 amu

ACTUAL MASS

mass of one atom or molecule in grams

C→$12 \times 1.66 \times 10^{-24}$ g

H_2O→$18 \times 1.66 \times 10^{-24}$ g

RELATIVE ATOMIC MASS OR RELATIVE MOLECULAR MASS

Mass of one atom or molecule w.r.t. $1/12^{th}$ of ^{12}C atom

C→ 12

H_2O → 18

It is unitless

GRAMS ATOMIC MASS OR GRAM MOLECULAR MASS

Mass of one mole of atom or molecule

C→ 12 g

H_2O → 18 g

It is also called molar weight

DEFINITION OF ONE MOLE

One mole is a collection of that many entities as there are number of atoms exactly in 12 g of C-12 isotope.

1u = 1 amu = $(1/12)^{th}$ of mass of 1 atom of C^{12} = $\frac{1g}{N_A}$ = 1.66×10^{-24} g

For elements

- 1 g atom = 1 mole of atoms = N_A atoms
- g atomic mass (GAM) = mass of N_A atoms in g.
- Mole of atoms = $\frac{\text{Mass(g)}}{\text{GAM or molar mass}}$

For molecule

- 1 g molecule = 1 mole of molecule = N_A molecule
- g molecular mass (GMM) = mass of N_A molecule in g.
- Mole of molecule = $\frac{\text{Mass(g)}}{\text{GMM or molar mass}}$

For ionic compounds

- 1 g formula unit = 1 mole of formula unit = N_A formula unit.
- g formula mass (GFM) = mass of N_A formula unit in g.
- Mole of formula unit = $\frac{\text{Mass(g)}}{\text{GFM or molar mass}}$

1 mole of substance

Contains 6.022×10^{23} particles

Weighs as much as molecular weight / atomic weight/ionic weight in grams

If it is a gas, one mole occupies a volume of 22.4 L at 1 atm & 273 K

Average or mean molar mass

The average molar mass of the different substance present in the container

$$M_{avg} = \frac{M_1n_1 + M_2n_2 + \ldots}{n_1 + n_2 + \ldots}$$

Here M_1, M_2 are molar mass of substances and n_1, n_2 are mole of substances present in the container.

DENSITIES

$$\text{Density} = \frac{\text{Mass}}{\text{volume}}, \text{ unit : g/cc}$$

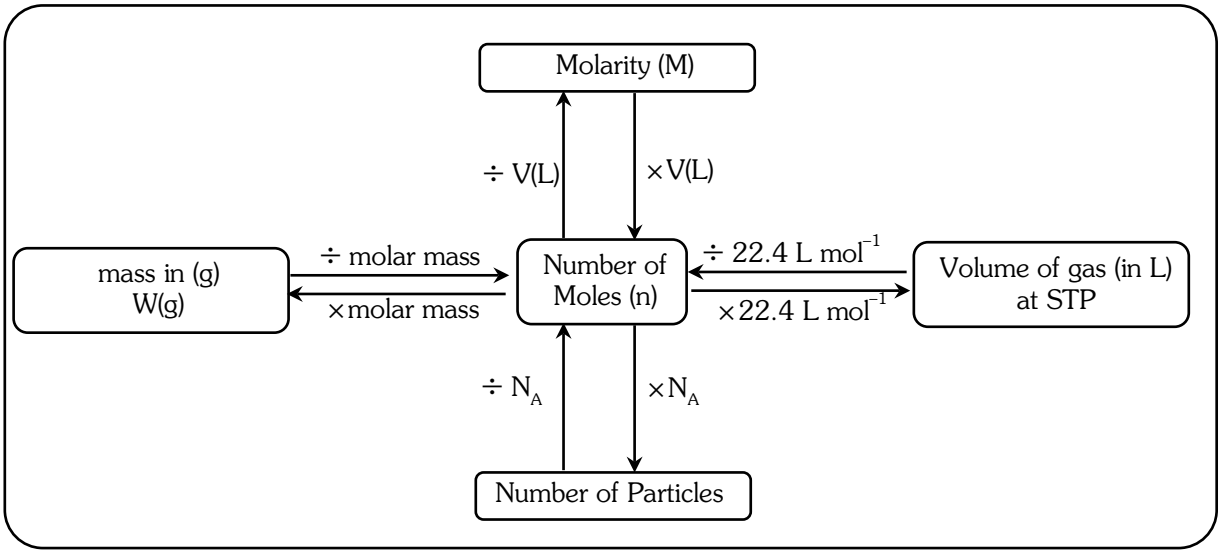
$$\text{Relative Density} = \frac{\text{Density of any substance}}{\text{Density of reference substance}}$$

VAPOUR DENSITY

Ratio of density of vapour to the density of hydrogen at similar pressure and temperature.

$$\text{Vapour density} = \frac{\text{Molar mass}}{2}$$

$$\text{mass \% of an element in a compound} = \frac{\text{atomicity of an element} \times \text{atomic mass of an element}}{\text{molecular mass of compound}} \times 100$$



❐ STOICHIOMETRY BASED CONCEPT

[Concept of limiting reagent]

$$aA + bB \rightarrow cC + dD$$

- a,b,c,d, represents the ratios of moles, volumes and pressure [for gaseous] and molecules in which the reactants react or products formed.
- a,b,c,d, does not represent the ratio of masses.

❐ HOW TO FIND L.R.

- **Case I** : If data of only one reactant is given then treat that reactant as L.R. and other reactants as excess reagent.
- **Case-II** : If data of more than one reactants are given then first convert all the data into moles then divide the moles of reactants with their respective stoichiometric coefficient. The reactant having minimum ratio will be L.R. then find the moles of product formed or excess reagent left by comparing it with L.R. through stoichiometric concept.

IMPORTANT NOTE

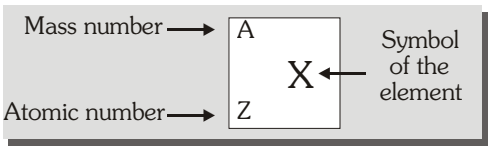
CHAPTER 02

ATOMIC STRUCTURE

IMPORTANT DEFINITIONS

Proton (m_p) /anode rays	**Neutron (m_n)**	**Electron(m_e) / cathode rays**
mass = 1.67×10^{-27} kg	mass = 1.67×10^{-27} kg	mass = 9.1×10^{-31} kg
mass = 1.67×10^{-24} g	mass = 1.67×10^{-24} g	mass = 9.1×10^{-28} g
mass = 1.00750 amu	mass = 1.00850 amu	mass = 0.000549 amu
Specific charge (e/m) value is dependent on the nature of gas taken in discharge tube.		**Specific charge (e/m)** of electron is found to be independent of nature of gas & electrode used.

REPRESENTATION OF AN ELEMENTS



Terms associated with elements :

- Atomic Number (Z) : = No. of protons

  No. of Electron = Z – C (charge on atom)
- Mass number (A) =Total number of neutron and proton present

  A = Number of proton + Number of Neutrons
- **Isotopes :** Same atomic number but different mass number

  Ex. : ${}_6C^{12}$, ${}_6C^{13}$, ${}_6C^{14}$
- **Isobars :** Same mass number but different atomic number

  Ex. ${}_1H^3$, ${}_2He^3$
- **Isoelectronic**:Species having same no. of electrons

  Ex. Cl^-, Ar, S^{2-}

ATOMIC MODELS

- **Thomson** : An atom considered to be positively charged sphere where e^- is embedded inside it.
- **Drawback** : Cannot explain stability of an atom.
- **Rutherford Model of an atoms :**
  Electron is revolving around the nucleus in circular path.
  $R_N = R_0(A)^{1/3}$, $R_0 = 1.33 \times 10^{-13}$ cm
  [A mass number, R_N = Radius of nucleus]

SIZE OF NUCLEUS

- The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.
- Thus, diameter of the atom is 10^5 times to the diameter of the nucleus and volume of atom is 10^{15} times to volume of nucleus.

ELECTROMAGNETIC SPECTRUM

- RW→MW→IR →Visible →UV →X-rays →CR (Radiowaves → Microwaves → Infrared rays →Visible rays →Ultraviolet rays →X-rays →Cosmic rays)
- Wavelength decreases ⟶
- Frequency and energy increases ⟶
- • $c=\nu\lambda$ • $\lambda = \frac{c}{\nu}$ • $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$
  • $T = \frac{1}{\nu}$ • $E = \frac{hc}{\lambda} = h\nu$, $h = 6.626 \times 10^{-34}$ Js
  • $E = \frac{12400}{\lambda(\text{Å})} \text{eV} = \frac{2 \times 10^{-25}}{\lambda(\text{m})}$
  • Total amount of energy transmitted $E = nh\nu = \frac{nhc}{\lambda}$
  n = number of photons

BOHR'S ATOMIC MODEL

Theory based on quantum theory of radiation and the classical laws of physics

- $\frac{K(Ze)(e)}{r^2} = \frac{mv^2}{r}$
- $mvr = \frac{nh}{2\pi}$ or $mvr = n\hbar$
- Electron remains in stationary orbit where it does not radiate its energy.
- **Radius :** $r = 0.529 \times \frac{n^2}{Z}$ Å
- **Velocity :** $v = 2.188 \times 10^6 \frac{Z}{n} ms^{-1}$
- Total energy (KE + PE) = $-13.6 \times \frac{Z^2}{n^2}$ eV/atom
- $TE = -\frac{KZe^2}{2r}$, $PE = \frac{-KZe^2}{r}$, $KE = \frac{KZe^2}{2r}$
  PE = −2KE, KE = −TE, PE = 2TE
- Revolutions per sec = $\frac{v}{2\pi r}$
- Time for one revolution = $\frac{2\pi r}{v}$
- Energy difference between n_1 and n_2 energy level

$$\Delta E = E_{n_2} - E_{n_1} = 13.6 \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \frac{eV}{atom} = IE \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where IE = ionization energy of single electron species.

- **Ionization energy** = $E_\infty - E_{G.S.} = 0 - E_{G.S.}$
  $E_{G.S.}$ = Energy of electron in ground state

HYDROGEN SPECTRUM

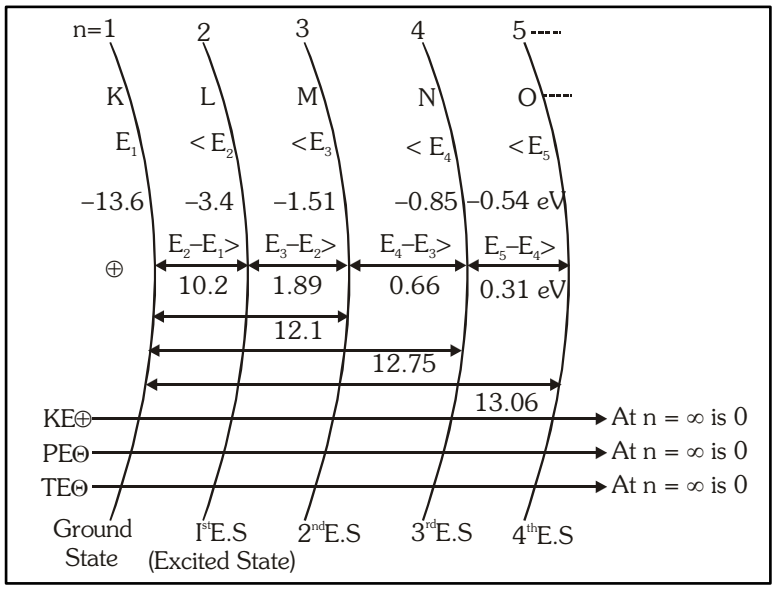
- **Rydberg's Equation** : $\frac{1}{\lambda} = \bar{\nu} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \times Z^2$

  $R_H \cong 109700\ cm^{-1}$ = Rydberg constant
- For first line of a series $n_2 = n_1 + 1$
- Limiting spectral line (series limit) means $n_2 = \infty$
- H_α line means $n_2 = n+1$; also known as line of longest λ, shortest ν, least energy
- Similarly H_β line means $n_2 = n_1 + 2$
- When electrons de-excite from higher energy level (n) to ground state in atomic sample, then number of spectral lines observed in the spectrum = $\frac{n(n-1)}{2}$
- When electrons de-excite from higher energy level (n_2) to lower energy level (n_1) in atomic sample, then number of spectral line observed in the spectrum

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

- No. of spectral lines in a particular series = $n_2 - n_1$

Hydrogen Spectrum	(n_2)		(n_1)
Lyman	→ Any higher orbit →	1	[Found in U.V. region]
Balmer	→ Any higher orbit →	2	[Found in Visible region]
Paschen	→ Any higher orbit →	3	[Found in I.R. region]
Brackett	→ Any higher orbit →	4	[Found in I.R. region]
Pfund	→ Any higher orbit →	5	[Found in I.R. region]



DE-BROGLIE HYPOTHESIS

- All material particles posses wave character as well as particle character.
- $\lambda = \frac{h}{mv} = \frac{h}{p}$
- The circumference of the n^{th} orbit is equal to n times of wavelength of electron i.e., $2\pi r_n = n\lambda$
  Number of waves = n = principal quantum number
- Wavelength of electron $(\lambda) \cong \sqrt{\frac{150}{V(volts)}}$ Å
- $\lambda = \frac{h}{\sqrt{2mKE}}$

HEISENBERG UNCERTAINITY PRINCIPLE

- According to this principle, "it is impossible to measure simultaneously the position and momentum of a microscopic particle with absolute accuracy"
  If one of them is measured with greater accuracy, the other becomes less accurate.
- $\Delta x.\Delta p \geq \frac{h}{4\pi}$ or $(\Delta x)(\Delta v) \geq \frac{h}{4\pi m}$
  where Δx = Uncertainity in position
  Δp = Uncertainity in momentum
  Δv = Uncertainity in velocity
  m = mass of microscopic particle
- Heisenberg replaced the concept of orbit by that of orbital.

QUANTUM NUMBER

In an atom each shell, subshell, orbital and electron are designated by a set of 4 quantum numbers.

- **Principal quantum number (By Bohr)**
  - ⇒ Indicates = Size and energy of the shell, distance of e^- from nucleus
  - ⇒ Values n = 1, 2, 3, 4, 5.....
  - ⇒ Angular momentum = $n \times \frac{h}{2\pi}$
  - ⇒ Total number of e^-s in a shell = $2n^2$
  - ⇒ Total number of orbitals in a shell = n^2
  - ⇒ Total number of subshell in a shell = n
- **Azimuthal/Secondary/Subsidiary/Angular momentum quantum number (ℓ)**
  - ⇒ Given by = Sommerfeld
  - ⇒ Indicates = Sub shells
  - ⇒ Values ⇒ 0, 1.....(n–1)
  - ⇒ Indicates shape of Sub shell

Value of n	Values of ℓ [Shape]	Initial from word
eg.	ℓ = 0 (s) [Spherical]	Sharp
If n = 4	ℓ=1 [p] [Dumb bell]	Principal
	ℓ=2 [d] [Double dumb bell]	Diffused
	ℓ=3 [f] [Complex]	Fundamental

  - ⇒ Total no. of e^- s in a sub shell = $2(2\ell + 1)$
  - ⇒ Total no. of orbitals in a sub shell = $(2\ell + 1)$
  - ⇒ Orbital angular momentum
  - ⇒ For H & H- like species all the subshells of a shell have same energy.

    i.e. 2s = 2p 3s = 3p = 3d
- **Magnetic quantum number (m_l)**
  - ⇒ Given by Linde
  - ⇒ Indicates orientation of orbitals i.e. direction of electron density.
  - ⇒ Value of m = $-\ell$ .....0.....$+\ell$
  - ⇒ Maximum no of e's in an orbital = 2 (with opposite spin)

    m for p sub shell = $\begin{matrix} p_x & p_y & p_z \\ -1 & +1 & 0 \end{matrix}$

    (There is no simple relation between value of m_l)

    m for d sub shell = $\begin{matrix} dxy & dyz & dz^2 & dxz & dx^2-y^2 \\ -2 & -1 & 0 & +1 & +2 \end{matrix}$
- **Spin quantum number (m_s or s)**

  Given by Uhlenback & Goudsmit

  Values of s = ±½

  Total value of spin in an atom = ±½×number of unpaired electrons

  Spin angular momentum = $\sqrt{s(s+1)}\frac{h}{2\pi}$

RULES FOR FILLING OF ORBITALS

- **Aufbau principle :** The electrons are filled up in increasing order of the energy in subshells.

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10}$$

- **(n + ℓ) rule :** The subshell with lowest (n + ℓ) value is filled up first, but when two or more subshells have same (n + ℓ) value then the subshell with lowest value of n is filled up first.
- **Pauli exclusion principle :** Pauli stated that no two electrons in an atom can have same values of all four quantum numbers.
- **Hund's rule of maximum multiplicity :** Electrons are distributed among the orbitals of subshell in such a way as to give maximum number of unpaired electrons with parallel spin.

- Schrödinger equation is written as $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system.
- The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as probability density and is always positive. From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found.

IMPORTANT NOTE

CHAPTER 03

CHEMICAL EQUILIBRIUM

- Equilibrium represents the state of a process in which the measurable properties like :- temperature, pressure, color, concentration of the system do not show any change with the passage of time.
- Equilibrium is a dynamic process, chemical equilibrium can be approached from both sides of reaction.
- The state of equilibrium is not affected by the presence of catalyst. It only helps to attain the equilibrium state in less or more time.
- Equilibrium can be attained both in homogeneous & heterogenous system.

Consider a reversible reaction,

$$aA + bB \underset{r_b}{\overset{r_f}{\rightleftharpoons}} cC + dD$$

AT EQUILIBRIUM STATE

Rate of forward reaction (r_f)

= rate of backward reaction (r_b)

So, at equilibrium,

$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_b}$; In terms of active mass

$K_P = \frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}$; In terms of partial pressure

$K_X = \frac{[X_C]^c[X_D]^d}{[X_A]^a[X_B]^b}$; In terms of mole fraction

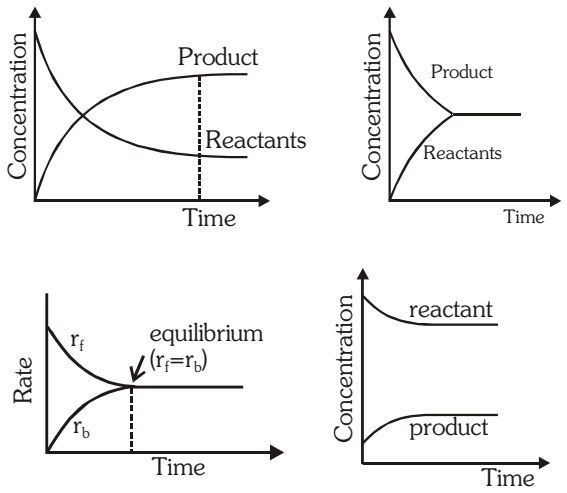
- The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.
- $K_P = K_C(RT)^{\Delta ng}$

  when $\Delta n_g = 0$ then $K_P = K_C$

  when $\Delta n_g > 0$ then $K_P > K_C$

  when $\Delta n_g < 0$ then $K_P < K_C$
- While determining Δn_g take only gaseous species.

GRAPHS



- **Unit of Equilibrium constant:**

  $K_C = (\text{mol } L^{-1})^{\Delta n_g}$; $K_P = (\text{atm})^{\Delta n_g}$

- **Application of K_c or K_P**
  - More is the value of K_P or K_C more is the extent of progress of reaction.
  - Stability of reactant increases when value of K decreases
  - Stability of Product increases when value of K increases.

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

✎ Equilibrium constant (k_{eq}) depends upon temperature.

Temperature :

Let K_1 & K_2 be equilibrium constant at T_1 & T_2 then

$$\text{Log}\left(\frac{K_2}{K_1}\right)=\frac{\Delta H^o}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

(Van't Hoff equation)

✎ **Mode of representation of reaction :**

For $A+B \rightleftharpoons C+D$ $K_c = K$ then

(a) $C+D \rightleftharpoons A+B$; $K'_C=\frac{1}{K}$

(b) $nA+nB \rightleftharpoons nC+nD$, $K''_C=K^n$

when n=2, then $K''_C=K^2$

$n=\frac{1}{3}$ then $K''_C=K^{1/3}$

(c) $A \rightleftharpoons B$ $K_C=K_1$

$B \rightleftharpoons C$ $K_C=K_2$

$C \rightleftharpoons D$ $K_C=K_3$ then

$A \rightleftharpoons D$ $K_C=K_1\times K_2\times K_3$

(d) $A \rightleftharpoons B$ $K_C=K_1$

$2C \rightleftharpoons 2B$ $K_C=K_2$

$D \rightleftharpoons C$ $K_C=K_3$ then

$A \rightleftharpoons D$ $K_C=\frac{K_1}{\sqrt{K_2}*K_3}$

✎ **Predicting the direction of reaction :**

Reaction Quotient (Q) is expressed in the same way as for equilibrium constant, except that the reaction may not necessarily be at equilibrium.

In general for the reversible reaction :

$aA + bB \rightleftharpoons cC + dD$

$$Q=\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$Q=\frac{[P_c]^c[P_D]^d}{[P_A]^a[P_B]^b}$$ (in terms of pressure)

If $Q = K_{eq}$ then system is in equilibrium

If $Q > K_{eq}$ then system proceed in backward direction to attain equilibrium.

If $Q < K_{eq}$ then system proceed in forward direction to attain equilibrium.

✎ **Degree of dissociation (α)**

$$\alpha=\frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$$

$$\alpha \propto (V)^{\frac{\Delta n_g}{\text{sum of stoichiometrics coefficients of gaseous products}}}$$

$$\alpha \propto \left(\frac{1}{P}\right)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficients of gaseous products}}}$$

PHYSICAL EQUILIBRIUM

Physical reaction :

Those reactions in which change in only & only physical states of substances takes place without any chemical change.

(i) Ice-water system (melting of ice) :

$$\underset{\text{(more volume)}}{Ice_{(s)}} + Heat \rightleftharpoons \underset{\text{(less volume)}}{water_{(\ell)}}$$

It is an endothermic process & there is decrease in volume. Thus, the favourable conditions for melting of ice are high temperature & high-pressure.

(ii) Water -Water vapour system (vapourisation of water) :

$$\underset{\text{(less volume)}}{water_{(\ell)}} \rightleftharpoons \underset{\text{(more volume)}}{vapour_{(g)}}$$

It is an endothermic process & there is increase in volume. Thus, the favourable conditions for vaporisation of water are high temperature, & low-pressure.

(iii) Solubility of gases in liquids :

$$Gas_{(g)} + water_{(\ell)} \rightleftharpoons Aqueous\ solution_{(\ell)}$$

It is an exothermic process, there is decrease in volume. Thus, low temperature and high pressure will favour the dissolution of a gas in liquid.

LE-CHATELIER'S PRINCIPLE

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

(Le-Chatelier's principle is applicable for both chemical and physical equilibrium)

CHEMICAL EQUILIBRIUM

S. No.	**Effect due to change in**		**$\Delta n_g = 0$** **$A \rightleftharpoons B$**	**$\Delta n_g > 0$** **$A \rightleftharpoons 2B$**	**$\Delta n_g < 0$** **$2A \rightleftharpoons B$**
a)	Concentration	(i) ↑ [A] (ii) ↓ [A]	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
b)	Pressure	(i) ↑ in pressure (ii) ↓ in pressure	Unchanged Unchanged	Backward direction Forward direction	Forward direction Backward direction
c)	Temperature	(i) ↑ in Endothermic (ii) ↑ in Exothermic	Forward direction Backward direction	Forward direction Backward direction	Forward direction Backward direction
d)	Dissociation	(i) ↑ in pressure (ii) ↑ in volume	Unchanged Unchanged	Dissociation Decreases Dissociation Increases	Dissociation Increases Dissociation Decreases
e)	Mixing of inert gas	(i) at constant P (ii) at constant V	Unchanged Unchanged	Dissociation Increases Unchanged	Dissociation Decreases Unchanged

IMPORTANT NOTE

CHAPTER 04

IONIC EQUILIBRIUM

ACID

Strong

$HClO_4$
HI
HBr
H_2SO_4
HCl
HNO_3

Weak

$HClO_3$
$HClO_2$
HClO
H_3PO_4
H_3PO_2
H_3PO_3
H_2S

H_2CO_3
HNO_2
H_2SO_3
HCN
H_3BO_3
HF
Almost all organic acid

Like : (acetic acid, oxalic acid)

BASE

Strong

Group-1 hydroxide
LiOH
NaOH
KOH
RbOH
Group-2 hydroxide
$Sr(OH)_2$
$Ba(OH)_2$

Weak

All other bases like
NH_4OH
$Zn(OH)_2$
$Al(OH)_3$
$Fe(OH)_3$
$Cu(OH)_2$
etc.

ARRHENIUS CONCEPT

Acid :

Which produce H^+ ion in aqueous solution.

e.g. HCl, H_2SO_4, $HClO_4$, H_3PO_4, CH_3COOH

but **H_3BO_3 is not a Arrhenius acid.**

Base :

Which produce OH^- ion in aqueous solution.

e.g. NaOH, $Mg(OH)_2$, $Ba(OH)_2$

Major Limitation :

Defined only in water solvent.

BRONSTED-LOWRY CONCEPT

Acid : Which gives H^+ in any solvent.

Base : which accepts H^+ in any solvent.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Conjugate Base}}{Cl^-} + \underset{\text{Conjugate Acid}}{NH_4^+}$$

- To find conjugate base of any Acid → Remove one H^+
- To find conjugate acid of any Base → add one H^+
- Water is Amphiprotic solvent (can accept as well as lose H^+)

$H_2O \rightleftharpoons H^+ + OH^-$ | $H_2O + H^+ \rightleftharpoons H_3O^+$

Major Limitation :

Does not explain acidic behaviour of aprotic acids

e.g. SO_2, SO_3, CO_2, $AlCl_3$, $SiCl_4$

OSTWALD'S DILUTION LAW

OSTWALD'S DILUTION LAW

(Only for weak electrolytes)

$\alpha \propto \sqrt{\text{dilution}}$; dilution $\uparrow \Rightarrow \alpha \uparrow$

EXPLANATION OF WATER

$H_2O \rightleftharpoons H^+ + OH^-$

K_w = Ionic product of water

$pK_w = pH + pOH$

K = dissociation constant of water

$K = \frac{K_w}{[H_2O]} \left[\because [H_2O] = 55.5\right]$

$K_W = [H^+][OH^-]$

FOR PURE WATER

1. $[H^+] = [OH^-]$
2. pH = pOH
3. $(PH)_{\text{pure water}} = \frac{PK_w}{2}$

- pH of an acidic solution is always less than pH of pure water.
- pH of an basic solution is always greater than pH of pure water.

DIFFERENT VALUES AT DIFFERENT TEMPERATURE

AT 25°C

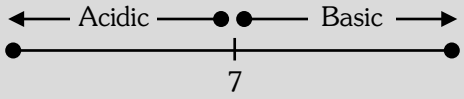
1. $K_W = 10^{-14}$
2. $(PH)_{\text{PURE WATER}} = (POH)_{\text{PURE WATER}} = 7$
3. PH + POH = 14

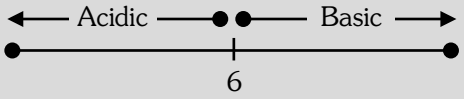
on increasing temperature $K_w \uparrow$

on increasing temperature $(pH)_{\text{pure water}}$ decreases

AT 90°C

1. $K_W = 10^{-12}$
2. $(PH)_{\text{PURE WATER}} = (POH)_{\text{PURE WATER}} = 6$
3. PH + POH = 12





pH of different solutions

Type I : Single Substance

CASE-1

Strong Acid :

$[H^+] = N_{Acid} + 10^{-7}$ (from water)

$pH = -\log [H^+]$

We neglect smaller values (in $N_{acid} + 10^{-7}$) if it is atleast 100 times smaller than other.

CASE-2

Strong Base :

$[OH^-] = N_{Base} + 10^{-7}$ (from water)

We can neglect smaller values. If it is atleast 100 times smaller than other.

$pOH = -\log [OH^-]$

$pH = pK_w - pOH$

CASE-3

Weak acid :

(for monobasic acid)

$[H^+] = \sqrt{K_a C}$

K_a = dissociation constant of acid

C : Initial concentation of acid

CASE-4

Weak base :

(for monoacidic base)

$[OH^-] = \sqrt{K_b C}$

K_b = dissociation constant of base

C : Initial concentration of base

Type II : More than one substances (Non-reacting)

CASE-5 : $(SA)_I + (SA)_{II}$

- Initially same Beaker (If individual volumes are not given): $[H^+] = N_1 + N_2$
- Initially in different beaker (Individual volumes are given): $[H^+] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

CASE-6 : $(SB)_I + (SB)_{II}$

- Same Beaker (Initially): $[OH^-] = N_1 + N_2$
- Different Beaker (Initially): $[H^-] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

CASE-7 : SA+WA or SB+WB

We can ignore $[H^+]$ / OH^- coming from weak part as compared to strong part due to common ion effect.

Type III : More than one substances (Reacting)

Case 8 : $\underset{N_1V_1}{SA} + \underset{N_2V_2}{SB} \rightarrow \text{Salt of SASB} + H_2O$

a) If $N_1V_1 = N_2V_2$

Then salt of SASB is left in beaker after reaction.

Salt of SASB :

- Does not hydrolyse
- Solution remain neutral (pH = 7 at 25°C)

b) If $N_1V_1 > N_2V_2$

Then SA + salt of SASB is left in solution among which only SA is the contributing substance towards pH.

$$[H^+] = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

c) If $N_1V_1 < N_2V_2$

Then SB + salt of SASB is left in solution among which only SB is contributing substance towards pH.

$$[OH^-] = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

Case 9 : $\underset{N_1V_1}{WA} + \underset{N_2V_2}{SB} \rightarrow \text{Salt of WASB} + H_2O$

a) If $N_1V_1 = N_2V_2$ [left :- salt of WASB]

Salt of WASB : Anionic hydrolysis

$$\Rightarrow K_h = \frac{K_w}{K_a};\ h = \sqrt{\frac{K_h}{C}}$$

$$\Rightarrow pH = 7 + \frac{1}{2}[pK_a + \log C] \quad (pH > 7)$$

b) If $N_1V_1 > N_2V_2$

[left : WA+ salt of WASB] **Acidic buffer**

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

Case 10 : $\underset{N_1V_1}{SA} + \underset{N_2V_2}{WB} \rightarrow \text{Salt of SAWB} + H_2O$

a) If $N_1V_1 = N_2V_2$ [left : salt of SAWB]

Salt of SAWB : Cationic hydrolysis

$$K_h = \frac{K_w}{K_b};\ h = \sqrt{\frac{K_h}{C}}$$

$$pH = 7 - \frac{1}{2}[pK_b + \log C];\ \ [pH < 7]$$

b) If $N_1V_1 < N_2V_2$

[left : WB + salt of SAWB] **basic buffer**

$$pOH = pK_b + \log\left(\frac{[salt]}{[base]}\right)$$

Case 11: $\underset{N_1V_1}{WA} + \underset{N_2V_2}{WB} \rightarrow \text{Salt of WAWB} + H_2O$

If $N_1V_1 = N_2V_2$ [left : salt of WAWB]

Salt of WAWB :

Cationic anionic or anionic cationic hydrolysis

$$K_h = \frac{K_w}{K_a \cdot K_b};\ h = \sqrt{K_h}$$

$$pH = 7 + \frac{1}{2}[pK_a - pK_b]$$

pH & h is independent of 'C'.

[pH can > 7, < 7 or = 7 depends on value of K_a & K_b]

Solubility(s) & Solubility Product (K_{sp})

Solubility :

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility(s). It is generally expressed in molarity.

$$AgCl_{(s)} \underset{\text{dissolution}}{\rightleftharpoons} AgCl_{(aq)} \underset{\text{dissociation}}{\longrightarrow} Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Solubility Product (K_{sp}) :

$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$

$K_{sp} = [Ag^{+}]\,[Cl^{-}]$

depends only on temperature.

Expressions of K_{sp} : $A_xB_y \rightleftharpoons xA^{+y} + yB^{x-}$

General form $K_{sp} = [A^{y+}]^x [B^{x-}]^y$

In terms of 'S' : $K_{sp} = (xS)^x (yS)^y$

$= x^x \cdot y^y \cdot (S)^{x+y}$

where s = solubility (in mol/litre)

Ionic Product [Q_{sp}]

$A_xB_y \rightleftharpoons xA^{+y} + yB^{x-}$; $Q_{ip} = [A^{y+}]^x [B^{x-}]^y$

In Q_{ip} the concentration taken are at any time but in K_{sp} the concentration are at equilibrium time / saturation time.

Applications :

1. If $Q_{ip} < K_{sp}$ [unsaturated]
2. If $Q_{ip} = K_{sp}$ [saturated]
3. If $Q_{ip} > K_{sp}$ [super saturated / ppt. will form]

Effect of common ion

- Presence of common ion decreases the solubility but has no effect on K_{sp} as it depends only on temperature.

Effect of odd ion

- Presence of odd ion increases the solubility but has no effect on K_{sp}.

Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
Methyl orange (MeOH)	Pinkish red	Yellow	3.1 to 4.5
Methyl red	Red	Yellow	4.2 to 6.2
Phenol red	Yellow	Red	6.2 to 8.2
Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

KEY POINTS

Buffer capacity

$$= \frac{\text{No. of moles of } H^{+}/OH^{-} \text{ added per litre}}{\text{change in pH of buffer solution}}$$

Maximum buffer action when [salt] = [acid]

pH of Amphiprotic species : (NaH_2PO_4, $NaHCO_3$) which can donate as well as accept H^+

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

CHAPTER 05

THERMODYNAMICS

DEFINITION

Deals with interaction of one body with another in terms of energy.

System : Part of universe under investigation

Surrounding : Rest part of universe except system.

Boundary : Which separates system & surrounding
- heat (q) and work (w) always appears at system boundary.

SYSTEM

Open	Closed	isolated
Energy and matter can exchange	Only energy can exchange	Neither energy nor matter

State function	Path function
Properties which depends only on initial & final state of system & not on process or path. e.g. U, H etc.	Depends on path or process, as well as intial and final state of the system. e.g. work, heat

THERMODYNAMIC PROPERTIES

Extensive	Intensive
Properties which are dependent of matter (size & mass) present in system e.g. Mass, volume, heat capacity etc.	Properties which are independent of matter (size & mass) present in system e.g. Pressure, temperature, Melting point, density etc.

PROCESSES

Isothermal	Isochoric	Isobaric	Adiabatic	Cyclic
T=const.	V=const.	P=const.	No heat exchange q = 0	Initial & final state of system are same

Reversible process	Irreversible process
• Slow process • At any time system and surrounding are in equilibrium. • $P_{sys} = P_{surr} \pm dP$	• Fast process • No equilibrium between system and surrounding • $P_{sys} = P_{surr} \pm \Delta P$

INTERNAL ENERGY (U) OR (E)

Sum of all molecular level energies. It is state function, depends on temperature and extensive property.

For Ideal gas : $\boxed{\Delta U = nC_V\Delta T}$

For chemical reaction :

$$\Delta_r E = \Sigma E_{prod} - \Sigma E_{react} \neq 0 \text{ at given T.}$$

HEAT (q)

Energy exchange due to temperature difference :

$q = C\Delta T$, $q = nC_m\Delta T$, $q = ms\Delta T$

C = heat capacity

C_m = molar heat capacity

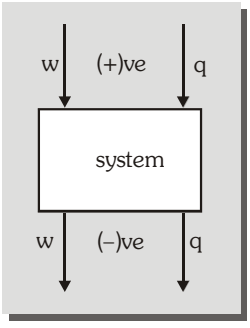
s = specific heat capacity

m = Amount of substance

WORK (W)

Reversible	Irreversible
$W_{rev} = -\int_{V_1}^{V_2} P_{ext} \cdot dV$	$W_{irr} = -P_{ext}(V_2 - V_1)$

SIGN CONVENTION



FIRST LAW OF THERMODYNAMICS (FLOT)

Law of conservation of energy

$\boxed{\Delta U = q + w}$

- Use proper sign convention of q and w.

WORK DONE IN VARIOUS PROCESS

Isochoric	Isobaric	Free expansion
$W = 0$	$W = -P_{ex}(V_2 - V_1)$	$P_{ext} = 0$
$\Delta U = q_V = nC_V\Delta T$	$q_P = nC_V\Delta T$	$W = 0, \Delta U = 0, q = 0$

Isothermal

$dT = 0$; $\Delta U = 0$ (for Inert gas); $q = -W$

Reversible Isothermal	Irreversible Isothermal
$W_{rev} = -nRT\ell n\left(\frac{V_2}{V_1}\right) = -nRT\ell n\left(\frac{P_1}{P_2}\right)$	$W_{irr} = -P_{ext}\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right]$

Adiabatic :

$q = 0 \quad \Rightarrow \Delta U = W = nC_V\Delta T \Rightarrow W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

$\gamma = \frac{C_P}{C_V} \quad \Rightarrow C_P$ = molar heat capacity at constant P.

$C_P - C_V = R \Rightarrow C_V$ = molar heat capacity at constant V.

For Reversible adiabatic :

PV^{γ} = constant (Ideal gas)

$TV^{\gamma-1}$ = constant (Ideal gas)

Enthalpy (H)

State function, extensive property, constant pressure, depend on temperature.

$H = U + PV$

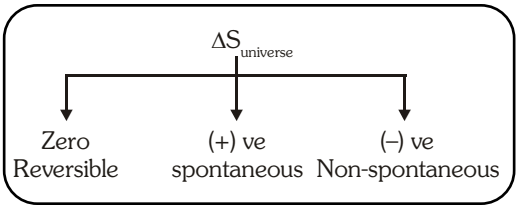
$\Delta H = nC_P\Delta T = q_P$ (Ideal gas)

For reaction : $\Delta H = \Delta U + \Delta n_g RT$

SECOND LAW OF THERMODYNAMICS (SLOT)

In an irreversible process (spontaneous process) entropy of universe increases.

$\Delta S_{system} + \Delta S_{surr} = \Delta S_{univ}$



ENTROPY(S)

State function, extensive property measurement of randomness a disorderness.

$S_{gas} > S_{liq} > S_{solid}$

$S\uparrow$ as temperature $\uparrow$; $\Delta S = \frac{q_{rev}}{T}$

$\Delta S = nC_V\ell n\left(\frac{T_2}{T_1}\right) + nR\ell n\left(\frac{V_2}{V_1}\right)$

$\Delta S = nC_P\ell n\left(\frac{T_2}{T_1}\right) + nR\ell n\left(\frac{P_1}{P_2}\right)$

Reversible phase transformation :

$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{MP}}$; $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{BP}}$

For chemical reaction :

$\Delta_r S = \sum S(\text{product}) - \sum S(\text{Reactant})$

Gibbs free energy (G) & spontaneity

G : State function; extensive property

$G = H - TS$

$\Delta G = \Delta H - T\Delta S$ (at constant T & P) $= -T(\Delta S)_{total}$

$\Delta G < 0$: Spontaneous process

$\Delta G = 0$: At equilibrium

$\Delta G > 0$: Non-spontaneous

ΔG: Measurement of Non-pV work (useful work)

$\Delta_r G = \sum \Delta_f G^0(\text{prod}) - \sum \Delta_f G^{\circ}(\text{react})$

$\Delta G = \Delta G^{\circ} + RT\ln Q$ (Rev. Rxn)

At equilibrium $\Delta G = 0$, $Q = K$

$\Delta G^{\circ} = -RT\ln K$

$\Delta_r H^{\ominus}$	$\Delta_r S^{\ominus}$	$\Delta_r G^{\ominus}$	Description
–	+	–	Reaction spontaneous at all temperatures
–	–	–	(at low T) Reaction spontaneous at low temp.
–	–	+	(at high T) Reaction non-spontaneous at high temp.
+	+	+	(at low T) Reaction non-spontaneous at low temp.
+	+	–	(at high T) Reaction spontaneous at high temp.
+	–	+	(at all T) Reaction non-spontaneous at all temp.

THERMOCHEMISTRY (ENERGETICS)

ENTHALPY OF REACTION (ΔH_R)

Amount of heat evolved or absorbed during a reaction at constant pressure.

ENTHALPY OF FORMATION ($\Delta_f H$) (May be endothermic or exothermic)

Change in enthalpy when one mole of a substance is formed from its constituent elements present in standard state.

For elements $\Delta_f H^\circ = 0$ (for standard state)

$\Delta_f H^\circ [O_2(g)] = 0, \quad (\Delta_f H^0)_{S_{8(rhombic)}} = 0$

$\Delta_f H^\circ [P_{4\ (white)}] = 0, \quad (\Delta_f H^0)_{C_{(graphite)}} = 0$

$$\Delta_r H^\circ = \sum \Delta_f H^\circ (prod.) - \sum \Delta_f H^\circ (react.)$$

ENTHALPY OF COMBUSTION ($\Delta_c H$) (always exothermic)

Change in enthalpy when 1 mole of a substance is completely burnt in oxygen.

$$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)\ ;\ \Delta_C H_{[C_2H_6(g)]}$$

$$\Delta_r H^\circ = \sum \Delta_C H^\circ (react.) - \sum \Delta_C H^\circ (prod.)$$

(When $\Delta_c H^0$ of each component in desried reaction is given)

$$\text{Calorific value} = \frac{\Delta H_{comb}}{\text{molecular wt}}$$

ENTHALPY OF TRANSITION

Enthalpy change when one mole of one allotropic form changes to another.

$$C_{(graphite)} \rightarrow C_{(diamond)} \quad \Delta_{tran} H^\circ = 1.9 \text{ kJ mol}^{-1}$$

$$H_2O_{(\ell)} \rightarrow H_2O_{(g)};\ \Delta_{vap} H^\circ (H_2O_{(\ell)})$$

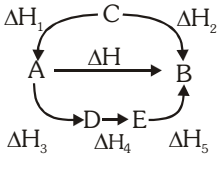
$$H_2O_{(S)} \rightarrow H_2O_{(\ell)};\ \Delta_{fus} H^\circ (H_2O_{(s)})$$

$$H_2O_{(S)} \rightarrow H_2O_{(g)};\ \Delta_{sub} H^\circ (H_2O_{(s)})$$

LAWS OF THERMOCHEMISTRY

(i) $A \rightarrow B \quad \Delta_r H = x \text{ kJ mol}^{-1}$
$B \rightarrow A \quad \Delta_r H = -x \text{ kJ mol}^{-1}$ } Lavoisier & Laplace law

(ii) Hess Law of Constant Heat summation



$\Delta H = \Delta H_1 + \Delta H_2$
or
$\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$
or
$\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$

BOND ENTHALPY (Always endothermic)

Average amount of enthalpy required to dissociate one mole gaseous bond into separate gaseous atoms.

$$\Delta_r H = \begin{pmatrix}\text{Sum of bond enthalpy}\\ \text{of gaseous reactant}\end{pmatrix} - \begin{pmatrix}\text{Sum of bond enthalpy}\\ \text{of gaseous product}\end{pmatrix}$$

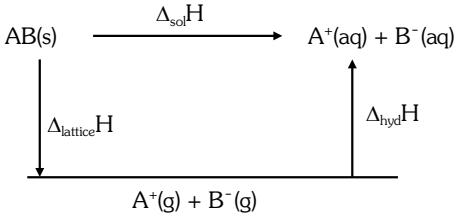
ENTHALPY OF ATOMISATION (ΔH_{atom}) (always endothermic)

Change in enthalpy when one mole of molecules converts into gaseous atoms.

Enthalpy of solution ($\Delta_{sol} H$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

The enthalpy of solution of AB(s), $\Delta_{sol} H$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice} H$ and enthalpy of hydration of ions, $\Delta_{hyd} H$ as $\Delta_{sol} H = \Delta_{lattice} H + \Delta_{hyd} H$



Enthalpy of dilution : It is the change in enthalpy when additional solvent is added to the solution. It depends on original concentration of solution and amount of solvent added.

$HCl(g) + 25\ aq. \rightarrow HCl.25\ aq.\ ;$
$\Delta H = -72.03 \text{ kJ / mol}$

$HCl(g) + 40\ aq. \rightarrow HCl.40\ aq.\ ;$
$\Delta H = -72.79 \text{ kJ / mol}$

ENTHALPY OF HYDRATION (ΔH_{hydra}) (always exothermic)

Enthalpy change when 1 mole of anhydrous salt combine with requisite amount of water to form hydrated salt.

$$\underset{\text{(anhy. salt)}}{CuSO_{4(s)}} + 5H_2O_{(\ell)} \rightarrow \underset{\text{(hydra.salt)}}{CuSO_4 .5H_2O_{(s)}};\ \Delta H^\circ_{hyd}$$

ENTHALPY OF HYDROGENATION (ΔH_{hydro}) (Always exothermic)

Enthalpy change during the complete hydrogenation of one mole unsaturated organic compound into its saturated compound.

$$\underset{(= \text{ or } \equiv \text{ bond})}{\text{unsaturated organic compound}} \xrightarrow{\Delta} \underset{(-\text{bond})}{\text{saturated organic compound}}$$

NOTE :

If in a reaction heat of reactant & products are given then heat of that reaction can be measured as follows:

(a) For heat of combustion & for bond enthalpy

$$\Delta_r H = \sum (\Delta H_C)_{reactant} - \sum (\Delta H_C)_{product}$$

$$\Delta_r H = \sum (B.E.)_{reactant} - \sum (B.E.)_{product}$$

(b) For heat of formation

$$\Delta_r H = \sum (\Delta H_f)_{product} - \sum (\Delta H_f)_{reactant}$$

IMPORTANT NOTE

CHAPTER 06

REDOX REACTION

"Those reactions is which oxidation and reduction occurs simultaneously known as redox reactions"

Oxidation state is the hypothetical or real charge which is produced upon an element due to electronegativity difference; in a compound.

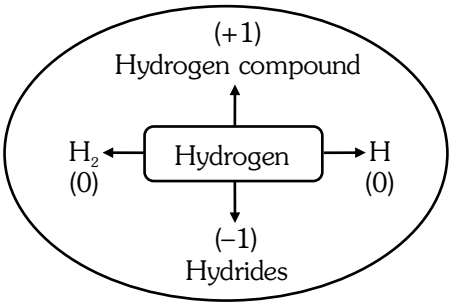
- A-A : OS of each A is zero
- A-B : OS of A is (–1) and B is (+1)

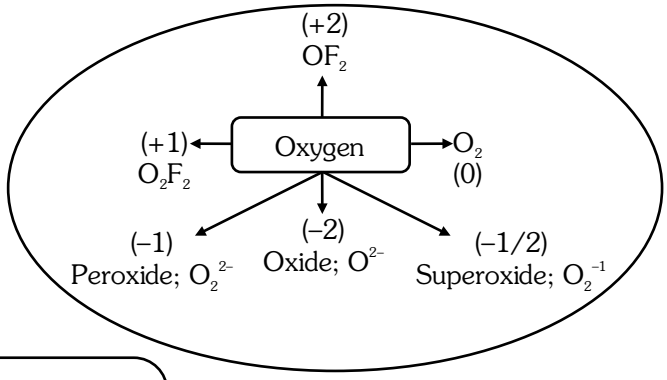
  $(EN)_A > (EN)_B$

To calculate oxidation state learn electronegativity order

P > H : S > C

C > H : Cl > N





Cu_2^{2+} : Oxidation state of Cu is (+1)

Hg_2^{2+} : Oxidation state of Hg is (+1)

OS of any atom may be zero, (+), (–), fractional number

OS of same atom may be different in different compounds

- In alloy, amalgam OS of element is zero. Example : (Na–Hg), (Brass), (Ni–Al)
- In allotropes OS of element is zero. Example : C_{gr}, C_{dia}
- In metal carbonyls OS of metal is zero. Example : $Ni(CO)_4$, $Fe(CO)_5$
- Sum of OS of each element in a compound is equal to zero

Example : H_2SO_4

$+1 \quad -2$

X

$2 \times 1 + X + 4 \times -2 = 0$

$\boxed{x = +6}$

- The oxidation state of central atom in its acid/radicals/salts and anhydrides are same.

Example : H_2SO_4 (Acid), $HSO_4^{\ominus}$ (Radical), SO_4^{2-} (Radical), Na_2SO_4 (Salt), $BaSO_4$ (Salt), SO_3 (Anhydride)

- **Oxidation number is the average of oxidation state.**

  Ca(OCl)Cl : OS of Cl = +1 – 1

  $$\text{O no. of Cl} = \frac{+1-1}{2} = 0$$

$Fe_3O_4 \rightarrow Fe_2O_3, FeO$

OS of Fe = +2, +3, +3

O no. of Fe = +8/3

$Pb_3O_4 \rightarrow 2PbO, PbO_2$

OS of Pb = +2, +2, +4

O no. of Pb = +8/3

For coordinate bond ($EN_B > EN_A$)

$\overset{+2}{A} \longrightarrow \overset{-2}{A}, \quad \overset{+2}{A} \longrightarrow \overset{-2}{B}, \quad \overset{0}{B} \longrightarrow \overset{0}{A}$

Applications of oxidation state :

☛

Highest Oxidation number	+1	+4	+2	+5	+7	+6	+7	+3	+8
Element	H	C	O	N	Cl	Cr	Mn	Fe	Os
Lowest oxidation number	–1	–4	–2	–3	–1	0	0	0	0

- A substance acts only as an **oxidising agent** if the oxidation number of one of its central element is in its highest oxidation state and as a **reducing agent** if the oxidation number of one of its central elements is in its lowest oxidation state. However, if the oxidation number of one of the elements of a substance is in its **intermediate oxidation state**, it can act **both as an oxidising as well as a reducing agent**.

  For example,

  - The O.N. of N in HNO_3, i.e. + 5 is the maximum, therefore, it can act only an oxidising agent by accepting one or more electrons. For example,

    $$I_2 + 10\overset{+5}{H}NO_3 \longrightarrow 2HIO_3 + 10\overset{+4}{N}O_2 + 4H_2O$$

    Here, the O.N. of N decreases from + 5 in HNO_3 to + 4 in NO_2 and hence it acts an oxidising agent.

  - The O.N. of S in H_2S, i.e., –2 is the minimum and hence it can act only as a reducing agent by losing one or more electrons. For example,

    $$Br_2 + \overset{-2}{H_2}S \longrightarrow \overset{0}{S} + 2HBr$$

    Hence the O.N. of S increase from –2 in H_2S to 0 in elemental sulphur and hence it acts as a reducing agent.

☛

Acidic strength $\propto$ OS of same central atom

Basic strength $\propto \frac{1}{\text{OS of different central atom}}$

☛ Valency factor = Change in oxidation number per unit formula
Valency factor of OA/RA = No. of e^- involved per unit formula
$= \frac{\text{No. of } e^- \text{ involved in balanced reaction}}{\text{Stoicheometric coefficient of OA/RA}}$

Valency factor of $KMnO_4$
(a) In acidic medium = 5
(a) In basic medium = 1
(c) In neutral medium = 3

☛ **Balancing of redox reactions**

(a) In acidic medium

Central atom
↓
Oxygen by addition of H_2O
↓
Hydrogen by addition of H^+
↓
Charge by addition of e^-

*Balance both half reactions individually and add in such a way number of e^- must be cancelled out.

(a) In basic medium

Central atom
↓
Oxygen by addition of H_2O
↓
Hydrogen by addition of H^+
↓
Removal of H^+ by addition of same OH^- both side
↓
Charge by addition of e^-

*Balance both half reactions individually and add in such a way number of e^- must be cancelled out.

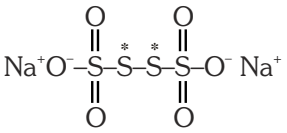
Stock notations Expressing the oxidation state of a metal by Roman numerals like I, II, III etc. within parenthesis is called Stock notation

e.g. $FeSO_4$ = Iron (II) sulphate;

Na_2CrO_4 = Sodium chromate (VI) etc.

SPECIAL FACTS

- In Fe_3O_4 i.e., FeO. Fe_2O_3 oxidation number of one Fe = + 2 while that of each of the other two=+3.
- In NH_4NO_3, oxidation no. of N of NH_4^+ = –3 while that of N in NO_3^- = + 5.
- In $Na_2S_4O_6$ (sodium tetrathionate) having the structure



The oxidation number of both S* is equal to 0 (pure covalent nature) and other to sulphur atoms have O.No. = +5

Redox couple is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half cell.

IMPORTANT NOTE

CHAPTER 07

CHEMICAL KINETICS

HOW TO GENERATE RATE LAW EXPRESSION

RATE OF REACTION

$n_1A + n_2B \rightarrow n_3C + n_4D$

rate

$$ROR = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \frac{1}{n_3}\frac{d[C]}{dt} = \frac{1}{n_4}\frac{d(D)}{dt}$$

*Rate of Disappearance of A=–d[A]/dt
*Rate of Disappearance of B=–d[B]/dt
*Rate of Appearance of C = +d[C]/dt
*Rate of Appearance of D = +d[D]/dt
*Unit of ROR = mol L^{-1} $time^{-1}$
*ROR is always positive.

Rate Law (Experimental Expression)
Rate = $K[A]^x[B]^y$

where, K = Rate constant or specific reaction rate.

x = order of reaction w.r.t. A
y = order of reaction w.r.t. B
x+y = n (overall order of reactions)

- Order is an experimental quantity
- It may be 'o', +ve, or fractional
- Unit of K = $[\text{mol } L^{-1}]^{1-n} \times \text{time}^{-1}$
  $= (\text{atm})^{1-n} \times \text{time}^{-1}$
  K depends upon temperature, catalyst & nature of reactant.

EXPERIMENTAL OBSERVATIONS

For the reaction $OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$ the experimental observations are given below

Exp.	$[OCl^-]$	$[I^-]$	$[OH^-]$	$d[IO^-]/dt$
1	0.0017	0.0017	1.0	1.75
2.	0.0034	0.0017	1.0	3.50
3.	0.0017	0.0034	1.0	3.50
4.	0.0017	0.0017	0.5	3.50

From experimental observations :
Rate law = $k[OCl^-][I^-]/[OH^-]$
Order =1

MOLECULARITY

- Molecularity is the total number of reacting species participating in an elementary reaction.
- It is a theoretical quantity & have only "integer values (i.e. 1,2,3).
- Molecularity >3 is very rare.

ELEMENTARY REACTIONS

These type of reactions complete in single step.

If $n_1A+n_2B \rightarrow$ Product
Rate law = $k[A]^{n1}[B]^{n2}$
Order = $(n_1 + n_2)$

- For elementary reaction fractional order is not possible.
- In elementary reaction molecularity is equal to its order.
- Zero order reactions can never be an elementary reaction.

PSEUDO FIRST ORDER REACTION

Reactions having order =1 and molecularity > 1
Eg. :
- **Hydrolysis of Ester in acidic medium.**
- **Inversion of cane sugar.**

Reactant taken in excess can't affect order of reaction

COMPLEX REACTIONS

These type of reactions complete in multi step :

Eg. : $2N_2O_5 \rightarrow 4NO_2 + O_2$

(i) $2N_2O_5 \rightleftharpoons 2NO_2 + 2NO_3$ (Fast)

(ii) $NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ (Slow)

(iii) $NO + NO_3 \rightarrow 2NO_2$ (Fast)

Here rate law is written in terms of slowest step (R.D.S.) which must be free from intermediates.

Rate law = $K[N_2O_5]$, Order =1

Molecularity of each reaction step is defined separately.

Total molecularity of complex reaction is not defined.

If not defined is not in the option then molecularity of the slowest step is equal to order of reaction. (Then in this case molecularity will be 1)

ZERO ORDER REACTIONS

E.g.: 1. Decomposition of Gases on metal surface.
2. Photochemical Reactions.
3. Enzyme catalysed reactions.

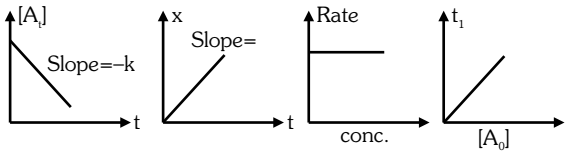
Differential Rate Equation :

$r = -d[A]/dt = k[A]^0$

Integrated Rate Equation

$[A]_t = [A]_0 - kt$; $x = kt$

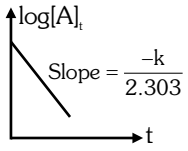
$$t_{1/2} = t_{50\%} = \frac{[A]_0}{2k}; \quad t_{100\%} = \frac{[A]_0}{k} = 2t_{1/2}$$

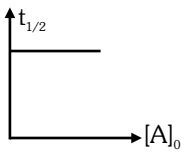


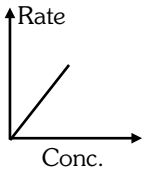
FIRST ORDER REACTION

Eg. 1. All Radioactive decay
2. Pseudo First order reaction.

Differential Rate Equation	Integrated Rate Equation
$r=-d[A]/dt = k[A]^1$	$kt = 2.303 \log \frac{[A]_0}{[A]_t}$







$t_{½} = t_{50\%} = \frac{0.693}{k}$

$t_{¾} = t_{75\%} = 2t_{½}$

N[th] ORDER REACTION

$$kt = \frac{1}{(n-1)}\left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right]; n \neq 1$$

$$kt_{1/2} = \frac{1}{(n-1)}\left[\frac{2^{n-1}-1}{[A]_0^{n-1}}\right]; n \neq 1$$

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

- It is half life method to determine order of reaction.
- Hydrolysis of ester in alkali medium is second order reaction.

Factors Affecting Rate of Reaction

- Nature of Reactant
- Radiation
- Concentration
- Pressure
- Catalyst
- Temperature

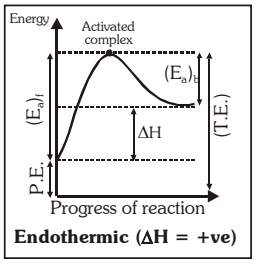
COLLISION THEORY

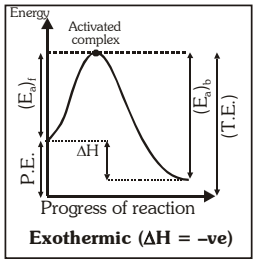
For Effective collision following two conditions must be satisfied :

(i) Reacting molecules must possess a minimum amount of energy known as Threshold Energy (TE)

(ii) Proper orientation of collision.

TE = Potential energy of reactant + Activation Energy (Ea)





$\Delta H = (E_a)_f - (E_a)_b = H_P - H_R$

Factors Affecting Activation Energy

(a) Nature of Reactant (b) Catalyst

Positive Catalyst⇒ ↓T.E. ⇒ ↓Ea ⇒↑Rate

Negative Catalyst⇒ ↑T.E.⇒ ↑Ea ⇒↓Rate

TEMPERATURE

a) Temperature coefficient (μ) :

By Default T = 25°C & m=2 is taken

$$\mu = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3$$

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{\Delta T/10}$$

(b) $k=Ae^{-Ea/RT}$ (Arrhenius Eq[n])

A = Arrhenius constant / Frequency factor / pre-exponential factor

Ea = Activation Energy

R = Gas Constant

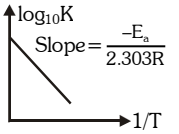
T = Temperature (K)

$e^{-Ea/RT}$ = Boltzmann factor

$k/A = e^{-Ea/RT}$ = Fraction of molecules having energy ≥ E_a

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$



IMPORTANT NOTE

CHAPTER 08

SOLUTIONS

Normality (N)
$= \frac{\text{No. of Gram Equivalents of solute}}{\text{Volume of solution (L)}}$

Molarity (M)
$= \frac{\text{No. of moles of solute}}{\text{Volume of solution (L)}}$

Relation b/w M&N
$N = M \times \text{Valency factor}$

% by Mass (w/w)
$= \frac{\text{Mass of solute (g)}}{\text{Mass of solution (g)}} \times 100$

Strength of solution (S)
$= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (L)}}$

Relation b/w m & X
$\frac{X_B}{X_A} = \frac{m \times (M.wt)_A}{1000}$

% mass by volume (w/v)
$= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100$

PPM (by mass)
$= \frac{\text{Mass of solute(g)}}{\text{Mass of solution(g)}} \times 10^6$

PPM (by volume)
$= \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 10^6$

PPM (by w/v)
$= \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 10^6$

COLLIGATIVE PROPERTY

Of dilute solution depends upon relative number of particles of solute & do not depend upon nature of solute particles.

Raoult's law

Liquid-Liquid System

Liquid : Volatile solvent (A) & volatile solute (B)

$P_A = X_A P_A^\circ$ & $P_B = X_B P_B^\circ$

$P_{total} = P_A + P_B = P^\circ_A X_A + P^\circ_B X_B$

$P_{total} = (P^\circ_B - P^\circ_A)X_B + P^\circ_A$

$P_A = Y_A P_T$ & $P_B = Y_B P_T$

(Dalton law for gaseous mixtures)

$P_A = P_A^\circ X_A = Y_A P_T$

$P_B = P^\circ_B X_B = Y_B P_T$

(Y_A & Y_B : mole fraction in vapour phase)

Solid-Liquid System

Solid : Non-volatile solute(B)

&

Liquid : Volatile solvent (A)

$P_{total} = P_A^\circ X_A = \frac{n_A}{n_A + n_B} \times P_A^\circ \ (\because P_B^\circ = 0)$

Relative lowering in vapour pressure

$(RLVP) = \frac{P^\circ_A - P_S}{P^\circ_A} = X_B$

Lowering of vapour pressure

$= \Delta P = P_A^\circ - P_S$

Derived from RLVP :

$\frac{P^\circ_A - P_S}{P_S} = \frac{n_B}{n_A}$

Van't Hoff Factor (i)

$\frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Caculated Molar Mass}}{\text{Observed Molar Mass}}$

For i=1 : Neither Association nor Dissociation

Eg. : Sugar, Glucose, Urea etc.

Dissociation (i>1)

$i = 1 + (n-1)\alpha$

n = total no. of ions

α = Degree of dissociation

Association (i>1)

$i = 1 - \alpha + \alpha/n$

n=No. of solute associated particles

α = Degree of Association

Relative Lowring of Vapour Pressure (RLVP)

For dilute solution ($n_B << n_A$)

$\frac{P^\circ_A - P_S}{P^\circ_A} \approx i \times \frac{n_B}{n_A}$

$\Delta P \propto \frac{n_B}{n_A}$

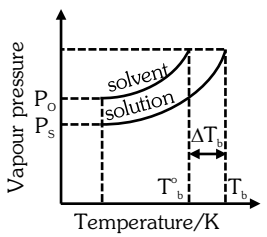
RLVP depends upon relative number of solute particles.

Elevation in Boiling Point (ΔT_b)

$\Delta T_b = (T_b)_{solution} - T_b^\circ = i \times m \times K_b$

K_b = molal elevation constant or ebullioscopic constant for a solvent

$K_f = \frac{RT_b^{\circ 2} \times (M.wt)_{Solvent}}{1000 \times \Delta H_{vapour}} \quad K_b = \frac{RT_b^{\circ 2}}{1000 \times L_{vapour}}$

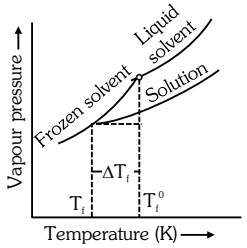


Depression in Freezing Point(ΔT_f)

$\Delta T_f = (T_f^\circ) - (T_f)_{solution} = i \times m \times K_f$

K_f = molal depression constant or Cryosopic constant for a solvent

$K_f = \frac{RT_f^{\circ 2} \times (M.wt)_{solvent}}{1000 \times \Delta H_{fusion}} \quad K_f = \frac{RT_f^{\circ 2}}{1000 \times L_{fusion}}$



Osmotic Presure (π)	**Osmosis :** Net flow of solvent molecules from dilute solution to concentrated solution through semi-permeable membrane. π = hdg For dilute solution : $\pi = i \times CRT$	**Isotonic solution :** $\pi_1 = \pi_2$ (Primary condition) At constant T; $i_1C_1 = i_2C_2$ (secondary condition)	**when $\pi_1 > \pi_2$ or $C_1 > C_2$** The solution 1 is called hypertonic solution solution 2 is called hypotonic solution.

% by Volume (v/v)

$$= \frac{\text{Volume of solute (mL)}}{\text{Volume of solution (mL)}} \times 100$$

Molality(m)

$$= \frac{\text{No. of moles of solute}}{\text{Amount of solvent (g)}} \times 1000$$

Volume Strength of H_2O_2 be 'XV'

$$M = \frac{X}{11.2};\ S = \frac{X}{5.2} \times 17$$

$$N = \frac{X}{5.6};\ \%(w/V) = \frac{X}{5.6} \times \frac{17}{10}$$

Molality(m) A → Solvent; B → Solute, Mole fraction

$$X_A = \frac{\text{Moles of solvent}}{\text{Moles of solute+Moles of solvent}} \quad X_B = \frac{\text{Moles of solute}}{\text{Moles of solute+Moles of solvent}}$$

$$X_A + X_B = 1$$

Dilution

$M_1V_1=M_2V_2$; $N_1V_1=N_2V_2$

I : When acid-acid or base-base mixed

$$N_R = \frac{N_1V_1 + N_2V_2 + N_3V_3 + ...}{V_1 + V_2 + V_3 + ...}$$

II : a) Complete Neutralisation

$N_AV_A = N_BV_B$ (A→Acid; B→Base)

$$N_R = \frac{N_AV_A}{V_A + V_B}$$

(N_R is the normality of salt)

b)Incomplete Neutralisation

$$N_R = \frac{|N_AV_A - N_BV_B|}{V_A + V_B}$$

Azeotropic Mixture : Binary mixtures having same composition in liquid & vapour phase & boil at a constant temperature. These mixtures are formed only by Non-ideal solutions. They are of two types a) **Minimum boiling azeotrope :** Show large positive deviation from Raoult's law. b) **Maximum boiling azeotrope :** Show large negative deviation from Raoult's law. Components of mixture can not be separated by fractional distillations.	**Reverse Osmosis :** When (External Pressure) > Osmotic Pressure then solvent molecules move from solution to solvent. Cryoscopic constant is maximum for camphor & it is the best solvent for determination of molar mass of solute by depression in freezing point.
Henrys Law : According to Henrys Law law at constant temperature. Partial pressure of Gas (P) ∝ Solubility of gas in liquid. Partial Pressure of Gas (P) ∝ Mole fraction of gas dissolved (X). $P = K_H \times X$ (K_H : Henry's constant) K_H depends upon natue of gas, temperature & nature of liquid $T\uparrow \Rightarrow K_H\uparrow$ Solubility (X)↓	Ethylene Glycol is usually added to water in the radiator to lower its freezing point. It is called anti-freeze. NaCl & $CaCl_2$ does the same work to clear shown from the roads. Gases which can react with solvent do not follow Henry's law.
Best method to determines molecular weight of macromolecules like protein is osmotic pressure because osmotic pressure can be easily measured at room temperature.	● 0.91% W/V NaCl solution is isotonic with blood. ● When density ≤ 1 ⇒ m > M (For a solution) When density >1 ⇒ m < M
● M, N, & % by volume, % w/v are temperature dependent terms. ● K_b & K_f are characteristics property of solvent.	35% (v/v) solution of ethyleneglycol, an antifreeze lower FP / water to 255.4K

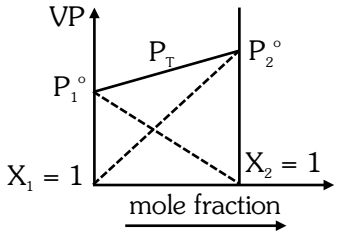
Ideal Solution

Obey Raoult's Law

$(VP)_{observed} = (VP)_{calculated}$

$(BP)_{observed} = (BP)_{calculated}$

(A–A) = (A–B) = (B–B)



$\Delta H_{mix} = 0$ $\Delta V_{mix} = 0$

$\Delta S_{mix} > 0$ $\Delta G < 0$

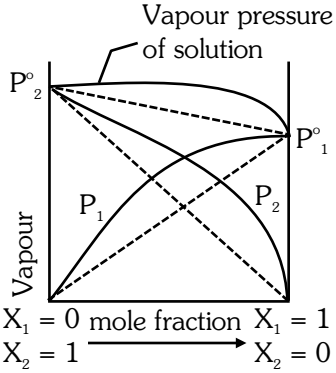
Non-Ideal Solution
Positive Derivation

Do not Obey Raoult's Law

$(VP)_{observed} > (VP)_{calculated}$

$(BP)_{observed} < (BP)_{calculated}$

(A–A) & (B–B) > (A–B)



$\Delta H_{mix} > 0$ $\Delta V_{mix} > 0$

$\Delta S_{mix} > 0$ $\Delta G < 0$

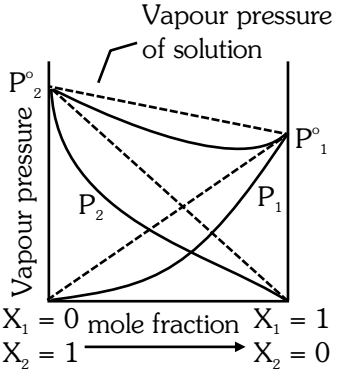
Non-Ideal Solution
Negative Derivation

Do not Obey Raoult's Law

$(VP)_{observed} < (VP)_{calculated}$

$(BP)_{observed} > (BP)_{calculated}$

(A-A) & (A–B) < (B–B)



$\Delta H_{mix} < 0$ $\Delta V_{mix} < 0$

$\Delta S_{mix} > 0$ $\Delta G < 0$

For all ideal and nonideal solutions $\Delta S_{mix} > 0$.

IMPORTANT NOTE

CHAPTER 09

ELECTROCHEMISTRY

Resistance

$(R) = \frac{V}{I}$

Unit of R : Ohms

SI based unit of R : Kgm^2/S^3A^2

Conductance $(G) = \frac{1}{R}$

Unit of G : mho, ohm^{-1} or Siemen's

Cell constant (G*) $= \frac{\ell}{A}$

Unit of G* : cm^{-1}

Resistivity or specific resistance (ρ)

$R = \rho\frac{\ell}{A}$

unit of ρ : ohm cm

Specific conductance / conductivity

$K(Kappa) = \frac{1}{\rho} = \frac{1}{R}\times\frac{\ell}{A} = G\times G^{*}C$

onductance of 1 cm^3 (m^3) solution of an electrolyte is called conductivity

Unit of K : ohm^{-1} cm^{-1}

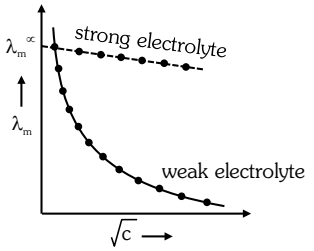
Debye-Huckel Onsager, Equation For strong electrolytes :

$\lambda_m = \lambda_m^{\infty} - A\sqrt{C}$

A : Debye Huckel Onsager constant.

c: Concentration

At constant temperature for a given solvent all electrolytes of same type have same 'A'.



GALVANIC CELL

Device in which spontaneous redox reaction ($\Delta G < 0$) is used to convert chemical energy into electrical energy.

Eg. : Daniel Cell

At anode : (–ve) oxidation $Zn(s) \rightarrow Zn^{+2}(aq) + 2e^-$

At cathode : (+ve) reduction $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s)$

Cell Reaction : $Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$

Current flow : Anode → Cathode (Internal circuit)

Cathode → Anode (External circuit)

- $[Zn^{+2}]$ ions in anode solution ↑
  $[Cu^{+2}]$ ions in cathode solution ↓
- Mass of Zn rod ↓ while mass of Cu rod ↑

Cell Representation :-

Anode	Anode half cell electrolyte (concentration)		Cathode half cell electrolyte (concentration)	Cathode
Zn(s)	$ZnSO_4$(aq) C_1M		$CuSO_4$(aq) C_2M	Cu(s

TRICK	
	L → Left
	O → Oxidation
	A → Anode
	N → Negative

E^{O}_{cell} = SRP (cathode) –SRP (anode)

Reduction Potential = –oxidation potential

NERNST EQUATION

- $E = E^0 - \frac{RT}{nF}\ell n\frac{[product]}{reactant}$
- At T = 298K $\Rightarrow E^0 = E^0 - \frac{0.0591}{n}\log_{10}\frac{[product]}{[reactant]}$
- For metals : If $[M^{n+}]\uparrow \Rightarrow E_{red}\uparrow \Rightarrow E_{oxid}\downarrow$
  If $[M^{n+}]\downarrow \Rightarrow E_{red}\downarrow \Rightarrow E_{oxid}\uparrow$
- $W_{electrical} = -\Delta G = +nFE_{cell}$
  If E_{cell} = +ve $\Rightarrow \Delta G$ = –ve $\Rightarrow$ Cell reaction is spontaneous
  If E_{cell} = –ve $\Rightarrow \Delta G$ = +ve $\Rightarrow$ Cell reaction is non-spontaneous
- At Equilibrium : $E_{cell} = 0 \Rightarrow \Delta G = 0$

  $E^{\circ}_{cell} = \frac{0.0591}{n}\log_{10} K_{eq}$

  [K_{eq} : Equilibrium constant]

  $\Delta G^{\circ} = -2.303\ RT\log_{10}K$
- Concentration cell : $E^{\circ}_{cell} = 0$

  $E_{cell} = -\frac{0.0591}{n}\log_{10}\frac{[product]}{[reactant]}$
- Electrode potential is an intensive property.
- In salt bridge, electrolytes used are KCl, KNO_3,NH_4NO_3 KCl/NaCl/NH_4Cl etc. cannot be used in salt bridge when solution contains Pb^{2+}, Hg_2^{2+}, Ag^+, Cu^+ because they react with Cl^- to form precipitate.

Molar conductance

$\Lambda_m = \mu = \Lambda_m = K \times V_m$

V_m =Molar volume in cm^3

unit of Λ_m =$ohm^{-1}cm^2\ mol^{-1}$

$$\Lambda_m = \frac{K \times 1000}{M}$$

Equivalent Conductance (λ_{eq} or Λ_{eq})

$$\Lambda_{eq} = K \times V = \frac{K \times 1000}{N}$$

Unit of $\Lambda_{eq} \rightarrow ohm^{-1}cm^2eq^{-1}$

Dilution ↑⇒ concertration↓

⇒ K↓ ⇒ (Λ_m,Λ_{eq})↑

Electrolytic Conductance↑

⇑

Solvation

Hydration of ions↓

(or)

Inter Ionic Interactions↓

(or)

Temperature↑

(or)

Dilution↑

Kohlrausch Law

$\Lambda_{eq} = \Lambda_{eq_c} + \Lambda_{eq_a}$

For A_xB_y : $A_xB_y \rightarrow xA^{y+} + yB^{x-}$

$\Lambda_m = x\Lambda_{m_c} + y\Lambda_{m_a}$

- $\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\infty}} = \frac{\Lambda_m}{\Lambda_m^{\infty}}$
- $K_a = \frac{c\alpha^2}{(1-\alpha)}$; If $\alpha \le 5\%$ then $K_\alpha = c\alpha^2$
- Λ_m(saturated) = $\Lambda_m^{\infty} = \frac{K \times 1000}{S}$

S → Solubility

ELECTROCHEMICAL SERIES

is the arrangement of elements in order of increasing standard reduction potential values

↓ Value of SRP increases.
Tendency to get reduce themselves↑
Oxidising Power ↑
Reactivity of metal ↓
Reactivity of non-metals/halogens ↑

↑ Value of SOP ↑
Tendency to get oxidise themselves ↑
Reducing Power ↑

- Oxidising Power α SRP α $\frac{1}{SOP}$ [Maximum SRP → F_2 (+2.87V)]
- Reducing Power α SOP α $\frac{1}{SRP}$ [Maximum SOP → Li (+3.05V)]
- Metals which are placed above in series can easily displace metal ion from their aqueous solutions which are placed below in series.

  $Cu + ZnSO_4(aq) \rightarrow$ No reaction

  $Cu + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2 + 2Ag(s)$
- Non-metals which are placed below in series can easily displace anions of non-metal from their aqueous solutions which are placed above in series.

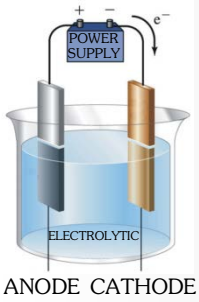
  $2A^- + B_2 \rightarrow 2B^- + A_2$

  $2C^- + B \rightarrow$ No reaction $\quad \boxed{E^\circ_{C^-/C_2} < E^\circ_{B^-/B_2} < E^\circ_{A^-/A_2} < E^\circ_{D^-/D_2}}$

  $2D^- + A_2 \rightarrow 2A^- + D_2$
- [Metals placed above H_2 / Metals placed above Mg / Metals from Mg to Cr / Metal Fe] $\xrightarrow{\text{displace}}$ [H_2(g) from aqueous solution of acid. / H_2(g) from cold water. / H_2(g) from hot water. / H_2(g) when react with steam.]
- Oxides of metal which are placed below to copper are thermally unstable & easily reduced to metal when heated.

$$Ag_2CO_3 \xrightarrow{\Delta} Ag_2O + CO_2 \uparrow$$
$$\downarrow$$
$$2Ag + ½O_2$$

Electrolytic Cell



- Device in which non-spontaneous redox reaction ($\Delta G>0$) is used to convert electrical energy into chemical energy.
- Cation (+ve) → Cathode (–ve) → Reduction
- Anion (–ve) → Anode (+ve) → Oxidation
- Sign of cathode & anode are opposite in Galvanic cell & Electrolytic cell.
- D.C. source is used for electrolysis.
- Efficiency of cell (η) $= \frac{\Delta G}{\Delta H} = \frac{-\eta FE}{\Delta H}$

Faraday's Law

Ist Law :

When electricity is passed through an electrolyte then $W \propto Q$; $W = Z \times i \times t$

Z (Electrochemical Equivalent):

Weight of substance in gram discharged by 1C charge

$$W = \frac{E \times i \times t}{96500}$$

IInd Law :

If same amount of charge is passed through different solution of electrolyte connects in series then

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \frac{W_4}{E_4} \text{...constant}$$

S.No.	Electrolyte	Electrode	Product at anode	Product at cathode	pH change
1.	Fused / molten NaCl	Pt or Graphite	Cl_2	Na	No change
2.	Aqueous NaCl	Pt or Graphite	Cl_2	H_2	pH↑
3.	Dilute NaCl	Pt or Graphite	O_2	H_2	No change
4.	Aqueous NaCl	Hg	Cl_2	Reduction of Na^+	No change
5.	Fused NaOH	Pt or Graphite	O_2	Na	No change
6.	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu	pH↓
7.	Aqueous $CuSO_4$	Cu	Cu oxidises to Cu^{+2}	Cu	No change
8.	Aqueous $CuCl_2$	Cu	Cu oxidises to Cu^{+2}	Cu	No change
9.	Aqueous $AgNO_3$	Pt or Graphite	O_2	Ag	pH↓
10.	Aqueous $AgNO_3$	Ag	Ag oxidises to Ag^+	Ag	No change
11.	Aqueous $NiSO_4$/$Ni(NO_3)_2$	Ni	Ni oxidises to Ni^{+2}	Ni	No change
12.	Aqueous $NiSO_4$	Pt or Graphite	O_2	Ni	pH↓
13.	Aqueous Na_2SO_4	Pt or Graphite	O_2	H_2	No change
14.	Dilute H_2SO_4	Pt or Graphite	O_2	H_2	No change

Corrosion

- Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.
- Rust is hydrated ferric oxide $Fe_2O_3.xH_2O$
- Factors which enhance corrosion are:
  (a) Presence of impurities in metal.
  (b) Presence of moisture (Eg. rainy season)
  (c) Presence of electrolyte. (Eg. Saline water)
- Corrosion can be prevented by Barrier protection (oil/grease), sacrificial protection (Galvanisation), Electrical protection.
- H_2–O_2 fuel cell was the source of drinking water & electrical energy in Appollo Moon flight.
- Mercury cell gives constant voltage throughout its life.
- Dry cell have short life because acidic NH_4Cl corrodes Zn container

Cell

- Primary cells cannot be recharged. Eg. Dry Cell & Mercury Cell
- Secondary cells can be recharged. Eg. Ni-Cd Cell & Lead storage battery.
- Fuel cell produce energy from the combustion of fuels which can be converted into electrical energy. Eg. : H_2-O_2 fuel cell.

Name of the cell/battery	Anode	Cathode	Electrolyte
Dry Cell	Zinc	Graphite; MnO_2+C (touching cathode)	$NH_4Cl + ZnCl_2$ (touching anode)
Mercury cell (used in watches, hearing aids)	Zinc-mercury Amalgum	Paste of HgO & carbon	Paste of KOH & ZnO
Lead storage battery	Lead	Lead Dioxide PbO_2	H_2SO_4 (38%)
Ni-Cd cell	Cadmium	$[Ni(OH)_3]$	KOH solution
H_2-O_2 fuel cell	Porous carbon containing catalysts (H_2 passed)	Porous carbon containing catalysts (O_2 passed)	Concentrated aq. NaOH solution

- Reactions in lead storage battery during discharge :
- At anode : $Pb_{(s)} + SO_4^{2-} \rightarrow PbSO_{4(s)} + 2e^-$
- At cathode : $4H^+ + PbO_{2(s)} + SO_4^{2-} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$
- Complete reaction : $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4 \rightarrow 2PbSO_{4(s)} + 2H_2O$
- Valency factor of H_2SO_4 in lead storage battery is 1.

- The EMF of a cell is found by adding oxidation potential & reduction potential of the half-cell reaction.
  $E^0_{cell} = \left(E^0_{OP}\right)_A + \left(E^0_{RP}\right)_C$; $E^0_{cell} = \left(E^0_{RP}\right)_C - \left(E^0_{RP}\right)_A$
- But the electrode potential of a half-cell from two other half cells cannot be found by simply adding their electrode potential so we use ΔG^0 data.

Given : 1) $Cu^{+2} + 2e^- \rightarrow Cu$, $E^\circ = 0.337V$
2) $Cu^{+2} + e^- \rightarrow Cu^+$, $E^\circ = 0.153V$
Aim : 3) $Cu^+ + e^- \rightarrow Cu$, $E^\circ = ?$

Subtracting 1-2 will not give the desired result. We have to calculate their free energy change.

Let ΔG°_1, ΔG°_2 & ΔG°_3 be free energy changes of the above three reactions. Then $\Delta G^\circ_1 - \Delta G^\circ_2 = \Delta G^\circ_3$

i.e. $(-2 \times F \times 0.337) - (-1 \times F \times 0.153) = -1 \times F \times E^\circ_{Cu+/Cu}$ ($\Delta G^\circ = -nFE^\circ$)

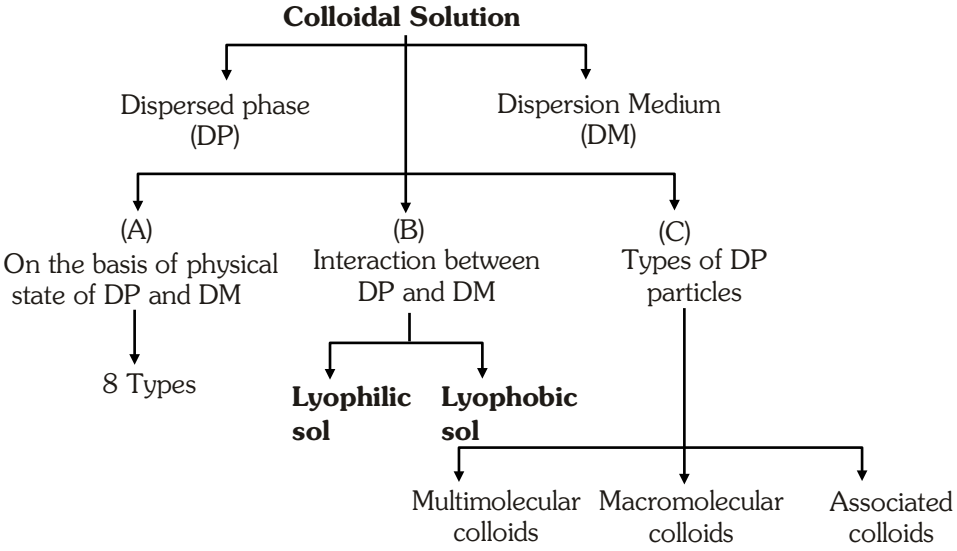
This gives $E^\circ_{Cu+/Cu} = 0.521$ V

CHAPTER 10

PREPARATION OF COLLIDAL SOLUTION

Colloids : Mixture are those having two or more than two components. If mixture is **homogenous**; it is known as **true solution** and it is **heterogeneous** is known as **colloidal solution**. Between two extremes of **suspension** and **solutions** we come across large group of systems called colloids.

- In colloids One substance has dispersed phase and another substance called dispersion medium.
- Colloidal particle size range from 1 to 1000 nm (10^{-9} to 10^{6} m)



- Depending upon nature of interaction between dispersed phase and dispersion medium, colloidal sols are of two types, **lyophilic (Solvent attracting)** and **lyophobic (Solvent repelling)**.

COMPARISION OF LYOPHOBIC AND LYOPHILIC SOLS

Property	Lyophilic sol (Emulsoid)	Lyophobic sol (Suspensoid)
1. Preparation	Can be easily prepared by shaking or warming the substance with liquid	Can not be prepared easily, special methods are required
2. Stability	are more stable due to excessive hydration	are less stable
3. Reversibility	are reversible because can be regenerated	are irreversible because can't be regenerated
4. viscosity	viscosity is much higher than that of dispersion medium	viscosity is nearly same as that of the dispersion medium
5. Surface tension	Surface tension is usually low	Surface tension is almost same as that of dispersion medium
6. Hydration or solvation	These are highly solvated as the particles have great affinity for solvent	These are less solvated as the particles have less affinity for the dispersion medium
7. Charge	The particles have little charge or no charge at all	The particles carry a characteristic charge either positive or negative
8. Visibility	Particles can not be seen under microscope	Particles can be seen under microscope
9. Tyndall effect	Less Scattering	More Scattering
10. Migration in electric field	may or may not migrate as they may or may not carry charge.	migrate towards anode or cathode as these particles carry charge.
11. General Ex.	**Mostly of organic nature** Ex. Gelatin, Starch, As_2S_3sol Gum, Albumin & Cellulose Solution	**Mostly of Inorganic nature** Ex. Transiton metal salt in water like Gold, As, $Al(OH)_3$sol, $Fe(OH)_3$sol etc.

The most common colloids are –

- **The Sols** (solids in liquids)
- **The gels** (liquids in solids)
- **The Emulsion** (liquids in liquids)
- If dispersion medium in water the sol is called **aqua sol**
- If dispersion medium is alcohol it is known as **alcosol**

- Lyophilic colloids can be prepared easily but special methods are required for lyphobic sols.

(+)ve charged lyophobic sols	(–)ve charged lyophobic sols
AgI/Ag^+	AgI/I^-
$Fe_2O_3 \cdot xH_2O/Fe^{+3}$	$Fe_2O_3 \cdot xH_2O/OH^-$

Preparation methods of colloidal solution

1. Peptization

The process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used is called a **Peptizing agent.**

Few examples of sols obtained by peptization :

(i) $AgI \downarrow + AgNO_3 \rightarrow [AgI]\, Ag^+ : NO_3^-$ **(ii)** $AgI \downarrow + KI \rightarrow [AgI]\, I^- : K^+$

(iii) $Fe(OH)_3 \downarrow + FeCl_3 \rightarrow [Fe(OH)_3]\, Fe^{3+} : 3Cl^-$ **(iv)** $Fe(OH)_3 \downarrow + NaOH \rightarrow [Fe(OH)_3]\, OH^- : Na^+$

(v) $CdS \downarrow + H_2S \rightarrow [CdS]\, S^{2-} : 2H^+$

The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added- particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

2. Chemical methods : The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided. **Some familiar reactions used are :**

(a) Double decomposition : A solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, then a stream of H_2S is passed through the solution. This is continued till an intense yellow coloured solution is obtained.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$
(excess) Yellow sol

(b) Oxidation : A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide or oxidising agent Ex.: HNO_3, Br_2, Etc.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S\ (Sol)$$

Sulphur sol can also be obtained when H_2S is bubbled through an oxidising agent (bromine water or nitric acid)

(c) Reduction : Colloidal solutions of metals like gold, silver, platinum, lead etc. can be obtained when their salts solutions are acted upon by reducing agents.

$$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au(Sol)$$

(d) Hydrolysis : Colloidal solution of many metal hydroxides are prepared by this method. Ferric hydroxide sol is prepared by the hydrolysis of ferric chloride with boiling water.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

The hydroxide sol of Cr and Al can also be prepared by this method.

Lab preparation of lyophilic & lyophobic sol

(a) Egg albumin sol

Prepare 100 mL of 5% (w/v) solution of NaCl in water in a 250 mL beaker.

↓

Break one egg in a porcelain dish and pipette out the albumin and pour it in sodium chloride solution. Stir well to ensure that the sol is well prepared.

(b) Starch/Gum sol

Measure 100 mL of distilled water with the help of a measuring cylinder and transfer it to a 250 mL beaker and boil it.

↓

Make a paste of 500 mg starch or gum in hot water and transfer this paste to 100 mL of boiling water with constant stirring. Keep water boiling and stirring for 10 minutes after addition of paste.

(c) Ferric hydroxide/Aluminium hydroxide (Lyophobic)

Take 100 mL of distilled water in a 250 mL beaker and boil it.

↓

Add 2g of ferric chloride/aluminium chloride powder to boiling water and stir it well.

↓

Take 100 mL of distilled water in another 250 mL beaker and boil it.

↓

Pour 10 mL of ferric chloride/aluminium chloride solution prepared drop by drop in the boiling water with constant stirring. Keep the water boiling till **brown/white** sol is obtained.

(d) Arsenious Sulphide sol

Take 100 mL of distilled water in a 250 mL beaker and boil it.

↓

Add 0.2 g of arsenious oxide to it and boil the content of the beaker.

↓

Cool and filter the solution.

↓

Pass H_2S gas through the filtered solution till it gives smells of H_2S. (**Kipp's apparatus**)

↓

Expel extra H_2S gas from the sol by slow heating and filter it.

↓

Label the filtrate as arsenious sulphide sol.

Process of conversion of colloidal solution in to precipitation by means of gravity is called **coagulation** it is main property of colloidal solution.

IMPORTANT NOTE

INORGANIC CHEMISTRY

CHAPTER 01

SOME IMPORTANT INCREASING ORDER

1. Acidic property

(i) SiO_2, CO_2, N_2O_5, SO_3

(ii) MgO, Al_2O_3, SiO_2, P_4O_{10}

(iii) HClO, $HClO_2$, $HClO_3$, $HClO_4$

(iv) CH_4, NH_3, H_2O, HF

(v) SiH_4, PH_3, H_2S, HCl

(vi) H_2O, H_2S, H_2Se, H_2Te

(vii) HF, HCl, HBr, HI

(viii) $lnCl_3$, $GaCl_3$, $AlCl_3$

(ix) BF_3, BCl_3, BBr_3, BI_3

2. Bond Angle

(i) CH_4, C_2H_4, C_2H_2

(ii) H_2O, NH_3, CH_4, CO_2

(iii) H_2O, NH_3, CH_4, BH_3

(iv) NO_2^-, NO_2, NO_2^+

(v) H_2Se, H_2S, H_2O

(vi) AsH_3, PH_3, NH_3

(vii) PF_3, PCl_3, PBr_3, PI_3

(viii) NF_3, NCl_3

(ix) NF_3, NH_3, NCl_3

(x) OF_2, OH_2, Cl_2O

3. Basic Character

(i) LiOH, NaOH, KOH, RbOH, CsOH
(ii) $Be(OH)_2$,$Mg(OH)_2$,$Ca(OH)_2$,$Ba(OH)_2$
(iii) BeO, MgO, CaO, SrO
(iv) NiO, MgO, SrO, K_2O, Cs_2O
(v) CO_2, B_2O_3, BeO, Li_2O
(vi) SiO_2, Al_2O_3, MgO, Na_2O
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) F^-, OH^-, NH_2^-, CH_3^-

4. Thermal Stability

(i) Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3
(ii) $BeCO_3$, $MgCO_3$, $CaCO_3$, $BaCO_3$
(iii) $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$,$Ba(OH)_2$

Polarisation

(iv) LiOH, NaOH, KOH, RbOH, CsOH
(v) $BeSO_4$, $MgSO_4$, $CaSO_4$
(vi) CsH, RbH, KH, NaH, LiH
(vii) SbH_3, AsH_3, PH_3, NH_3
(viii) H_2Te, H_2Se, H_2S, H_2O
(ix) HI, HBr, HCl, HF

5. Ionic Character

(i) LiBr, NaBr, KBr, RbBr, CsBr

(ii) LiF, NaF, KF, RbF, CsF

(iii) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

(iv) BCl_3, $AlCl_3$, $GaCl_3$

(v) VCl_4, VCl_3, VCl_2

(vi) AlF_3, MgF_2, NaF

(vii) AlN, Al_2O_3, AlF_3

(viii) HI, HBr, HCl, HF

(ix) CuCN, AgCN

(x) AgCl, KCl

6. Atomic / Ionic Size

(i) Mg^{2+}, Na^+, F^-, O^{2-}, N^{3-} (Hint : Isoelectronic series

(ii) Ca^{2+}, Ar, Cl^-, S^{2-}

(iii) O, C, S, Se

(iv) B, Be, Li, Na

(v) F, O, F^-, O^{2-}

7. Oxidizing Power

(i) $Cr_2O_7^{2-}$, MnO_4^-

(ii) MnO_4^{2-}, MnO_4^-

(iii) WO_3, MoO_3, CrO_3

(iv) $GeCl_4$, $SnCl_4$, $PbCl_4$

(v) I_2, Br_2, Cl_2, F_2

(vi) Zn^{+2}, Fe^{+2}, Pb^{2+}, Cu^{2+}, Ag^+

8. Ionization Energy

(i) Na, Al, Mg, Si

(ii) Li, B, Be, C, O, N, F, Ne, He (I^{st} I.P.)

(iii) Be, C, B, N, F, O, Ne, Li, He (II^{nd} I.P.)

9. Melting Point

(i) Cs, Rb, K, Na, Li
(ii) Mg, Ba, Sr, Ca, Be
(iii) CaI_2, $CaBr_2$, $CaCl_2$, CaF_2
(iv) $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$
(v) NaI, NaBr, NaCl, NaF
(vi) CsCl, RbCl, KCl, NaCl
(vii) $AlCl_3$, $MgCl_2$, NaCl

10. Boiling Point

(i) PH_3, AsH_3, NH_3, SbH_3
(ii) H_2S, H_2Se, H_2O
(iii) HCl, HBr, HI, HF
(iv) NH_3, HF, H_2O
(v) He, Ne, Ar, Kr
(vi) H_2O, D_2O
(vii) H_2, Cl_2, Br_2

11. Extent of Hydrolysis

(i) CCl_4, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_5
(ii) $BiCl_3$, $SbCl_3$, $AsCl_3$, PCl_3, NCl_3

12. Bond Strength

(i) HI, HBr, HCl, HF
(ii) $-\overset{\diagdown}{\underset{\diagup}{C}}-I$, $-\overset{\diagdown}{\underset{\diagup}{C}}-Br$, $-\overset{\diagdown}{\underset{\diagup}{C}}-Cl$, $-\overset{\diagdown}{\underset{\diagup}{C}}-F$
(iii) N – N, N = N, N ≡ N
(iv) As – H, Sb – H, P – H, N – H
(v) N_2^{2-}, N_2^-, N_2^+, N_2
(vi) O_2^{2-}, O_2^-, O_2 , O_2^+, O_2^{2+}

LiI, LiBr, LiCl, LiF, NaI, NaBr, NaCl, NaF, CsCl, RbCl, KCl, NaCl BaO, SrO, CaO, MgO

(vii) F_2, H_2, O_2, N_2
(viii) NO^-, NO, NO^+
(ix) I_2, F_2, Br_2, Cl_2
(x) O–O, S– S
(xi) F – F, O – O, N – N, C – C, H – H

13. Reducing Power

(i) $PbCl_2$, $SnCl_2$, $GeCl_2$
(ii) HF, HCl, HBr, HI
(iii) Ag, Cu, Pb, Fe, Zn
(iv) HNO_3, H_2SO_3, H_2S
(v) H_3PO_4, H_3PO_3, H_3PO_2

14. Covalent Character

(i) LiCl, $BeCl_2$, BCl_3, CCl_4
(ii) $SrCl_2$, $CaCl_2$, $MgCl_2$
(iii) $TiCl_2$, $TiCl_3$, $TiCl_4$
(iv) LiCl, LiBr, LiI
(v) Na_2O, Na_2S
(vi) AlF_3, Al_2O_3, AlN
(vii) HF, HCl, HBr, HI

15. Strength of Hydrogen bonding (X...H–X)

(i) S, Cl, N, O, F
(ii) NH_3, H_2O, HF

16. Ionic Radii in water

(i) Cs^+, Rb^+, K^+, Na^+, Li^+
(ii) Li^+, Be^{+2}
(iii) Na^+, Mg^{+2}, Al^{+3}

17. Hydration of Ions/Hydration Energy

(i) Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, Be^{+2}
(ii) Cs^+, Rb^+, K^+, Na^+, Li^+
(iii) Na^+, Mg^{+2}, Al^{+3}

18. Electron Affinity

(i) I, Br, F, Cl
(ii) O, S, F, Cl
(iii) N, P, O, S

19. Electronegativity

(i) As, P, S, Cl (ii) I, Br, Cl, F (iii) C, N, O, F

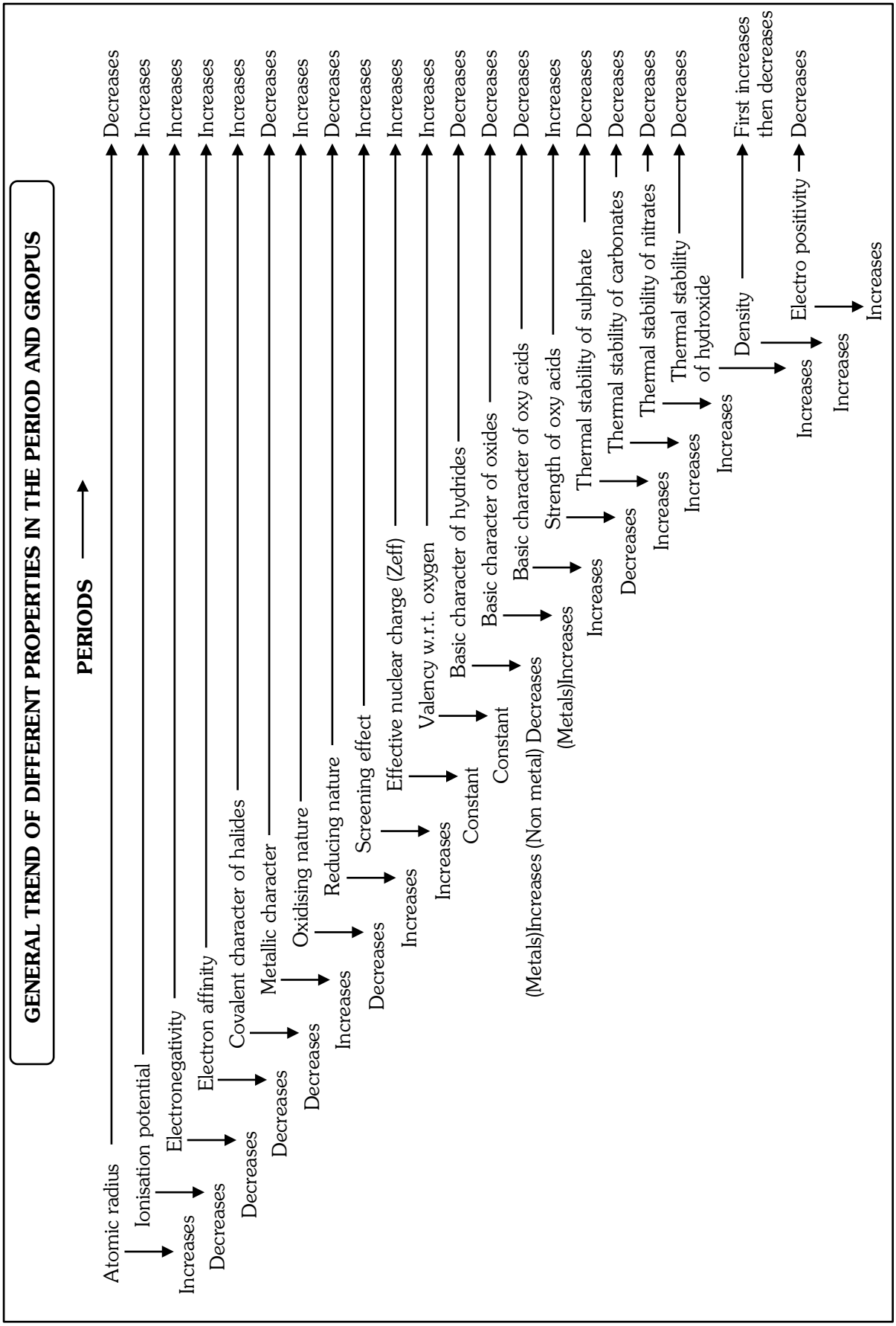
20. Bond Length

(i) N_2, O_2, F_2, Cl_2
(ii) N≡N, C≡N, C≡C
(iii) CO, $\overset{\diagdown}{\underset{\diagup}{C}}=O$, $-\underset{|}{\overset{|}{C}}-O-$
(iv) NO^+, NO, NO^-
(v) O_2, O_3, H_2O_2 (O-O bond length)
(vi) CO, CO_2, CO_3^{-2}
(vii) N_2, N_2^-, N_2^{-2}
(viii) O_2^{+2}, O_2, O_2^-, O_2^{-2}
(ix) HF, HCl, HBr, HI

21. Dipole moments

(i) CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl
(ii) NF_3, NH_3, HF, H_2O
(iii) Cis-chloropropene, Trans-chloropropene
(iv) p, m, o-dichlorobenzene
(v) CH_3I, CH_3Br, CH_3F, CH_3Cl
(vi) NH_3, SO_2, HF, H_2O
(vii) H_2S, H_2O
(viii) HI, HBr, HCl, HF
(ix) PH_3, ASH_3, SbH_3, NH_3
(x) H_2O, H_2O_2

SOME IMPORTANT INCREASING ORDER



IMPORTANT NOTE

Extended or Long Form of the Periodic Table

s-Block Elements | p-Block Elements | d-Block Elements | f-Block Elements

Metals | Non metals | Metalloids

Period ↓ / Group →	IA (1)		IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	(8)	VIII (9)	(10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	0 (18)
1	**1** H 1.0079 Hydrogen																	**2** He 4.0026 Helium
2	**3** Li 6.940 Lithium	**4** Be 9.0122 Beryllium											**5** B 10.811 Boron	**6** C 12.011 Carbon	**7** N 14.007 Nitrogen	**8** O 15.999 Oxygen	**9** F 18.998 Fluorine	**10** Ne 20.180 Neon
3	**11** Na 22.990 Sodium	**12** Mg 24.305 Magnesium											**13** Al 26.982 Aluminium	**14** Si 28.086 Silicon	**15** P 30.974 Phosphorus	**16** S 32.066 Sulphur	**17** Cl 35.453 Chlorine	**18** Ar 39.948 Argon
4	**19** K 39.098 Potassium	**20** Ca 40.078 Calcium	**21** Sc 44.956 Scandium	**22** Ti 47.867 Titanium	**23** V 50.941 Vanadium	**24** Cr 51.996 Chrominum	**25** Mn 54.938 Manganese	**26** Fe 55.847 Iron	**27** Co 58.933 Cobalt	**28** Ni 58.693 Nickel	**29** Cu 63.546 Copper	**30** Zn 65.39 Zinc	**31** Ga 62.723 Gallium	**32** Ge 72.61 Germanium	**33** As 74.922 Arsenic	**34** Se 78.96 Selenium	**35** Br 79.904 Bromine	**36** Kr 83.80 Krypton
5	**37** Rb 85.468 Rubidium	**38** Sr 87.62 Strontium	**39** Y 88.906 Yttrium	**40** Zr 91.224 Zirconium	**41** Nb 92.906 Niobium	**42** Mo 95.94 Molybdenum	**43** Tc 98 Technetium	**44** Ru 101.07 Ruthenium	**45** Rh 102.91 Rhodium	**46** Pd 106.42 Palladium	**47** Ag 107.87 Silver	**48** Cd 112.41 Cadmium	**49** In 114.82 Indium	**50** Sn 118.71 Tin	**51** Sb 121.76 Antimony	**52** Te 127.60 Tellurium	**53** I 126.90 Iodine	**54** Xe 131.29 Xenon
6	**55** Cs 132.91 Cesium	**56** Ba 137.33 Barium	**57** La* 138.91 Lanthanum	**72** Hf 178.49 Hafnium	**73** Ta 180.95 Tantalum	**74** W 183.84 Tungsten	**75** Re 186.21 Rhenium	**76** Os 190.23 Osmium	**77** Ir 192.22 Iridium	**78** Pt 195.08 Platinum	**79** Au 196.97 Gold	**80** Hg 200.59 Mercury	**81** Tl 204.38 Thallium	**82** Pb 207.2 Lead	**83** Bi 208.98 Bismuth	**84** Po 210 Polonium	**85** At 210 Astatine	**86** Rn 222 Radon
7	**87** Fr 223 Francium	**88** Ra 226 Radium	**89** Ac** 227 Actinium	**104** Rf 261 Rutherfordium	**105** Db 262 Dubnium	**106** Sg 266 Seaborgium	**107** Bh 264 Bohrium	**108** Hs 269 Hassium	**109** Mt 268 Meitnerium	**110** Ds 269 Darmstadtium	**111** Rg 272 Roentgenium	**112** Cn 277 Copernicium	**113** Nh Nihonium	**114** Fl Flerovium	**115** Mc Moscovium	**116** Lv Livermorium	**117** Ts Tennesine	**118** Og Oganesson

6	*Lanthanide Series	**58** Ce 140.12 Cerium	**59** Pr 140.91 Praseodymium	**60** Nd 144.24 Neodymium	**61** Pm 145 Promethium	**62** Sm 150.36 Samarium	**63** Eu 151.96 Europium	**64** Gd 157.25 Gadolinium	**65** Tb 158.93 Terbium	**66** Dy 162.50 Dysprosium	**67** Ho 164.93 Holmium	**68** Er 167.26 Erbium	**69** Tm 168.93 Thulium	**70** Yb 173.07 Ytterbium	**71** Lu 174.97 Lutetium
7	**Actinide Series	**90** Th 232.04 Thorium	**91** Pa 231.04 Protactinium	**92** U 238.03 Uranium	**93** Np 237 Neptunium	**94** Pu 244 Plutonium	**95** Am 243 Americium	**96** Cm 247 Curium	**97** Bk 247 Berkelium	**98** Cf 251 Californium	**99** Es 252 Einsteinium	**100** Fm 257 Fermium	**101** Md 258 Mendelevium	**102** No 259 Nobelium	**103** Lr 262 Lawrencium

IUPAC designations of groups of elements are given in brackets

DEVELOPMENT OF PERIODIC TABLE

- Prout's Hypothesis
- Dobernier's triad
- Newlands law of octave
- Lother meyer curve

MENDELEEV'S PERIODIC TABLE

Base chemical properties of elements.
Like : reaction with O_2, H_2 & X_2

Mendeleev's Periodic Law
Physical & chemical properties of elements are periodic function of their atomic weight

8 Groups & 7 period

Left some vacant position for some elements.

eka-boron - Sc
eka-Aluminium-Ga
eka-managanse-Tc
eka-silicon-Ga

MOSELEY X-RAY EXPERIMENT $Z \propto V$

Modern Periodic law
Physical & chemical properties of the elements are periodic function of their atomic numbers.
Introduced zero group for Nobel gases.

DIVISION OF ELEMENTS ON SPECIFIC GROUNDS

(a) Bohr classification

(i) Normal/representative elements s & p block (except inert gas) ns^{1-2} np^{1-5}; use electrons only valence shell during chemical combination.

(ii) Transition elements

d-block : use electrons of n shell as well as (n—1) shell during chemical combination.

Zn, Cd & Hg and Cn are not transitional elements.

(iii) Inner transition elements

f-block : use electrons of n shell (n-1) shell and (n-2) shell

(iv) **Inert gases :**

18 group He, Ne, Ar, Kr, Xe, Rn

Do not use any electron during chemical combination

(b) **On the basis of conductivity**

Metal → conductor

Metalloid → semi-conductor

Non-metals → Non-conductor

(c) **On the basis of physical state**

Solid (rest)

Liquid (6): Br, Ga, Hg, Uub, Cs, Fr

Gas (12): He, Ne, Ar, Kr, Xe, Rn, F, Cl, O, N, H, Og

POSITION OF ELEMENTS IN PERIODIC TABLE

- Period : Highest number of shell, which contain electron.
- Block : Highest energy sub-shell which contain electron.

$ns < (n-2)\,f < (n-1)d < np$

- Group No. :

depends on block

(a) s-block : Number of ns electron's

(b) p-block : Number of np electron's +12

(c) d-block : Number of ns + (n-1)d electron's

(d) f-block : 3rd or IIIB group.

Eg. :
Atomic number 53:
[Kr] $5s^2\ 4d^{10}\ 5p^5$
Period-5
Block-P
Group- 12 + 5 = 17

PERIODICITY

Repetition of properties after regular interval is known as periodicity and these properties are known as periodic properties.

1. Effective nuclear charge (Z_{eff})
2. Atomic Radius
3. Ionisation potential
4. Electron affinity
5. Electro negativity

SCREENING EFFECT / SHIELDING EFFECT

Repulsive force applied by inner electron on a particular electron / last electron / tested electron.

Calculation of screening (σ)- by Slater's Rule.

σ by test electron = 0.00

σ by rest of valence electron = 0.35

σ by (n-1) s,p → 0.85

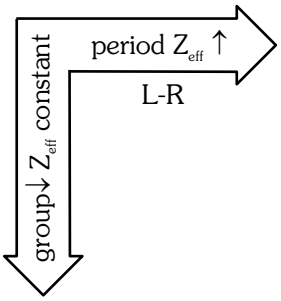
σ by (n-2) or inner electrons = 1.0

Varation of σ → along the periodic & down the group increases.

Order of σ : s > p > d > f

Effective nuclear charge (Z_{eff})

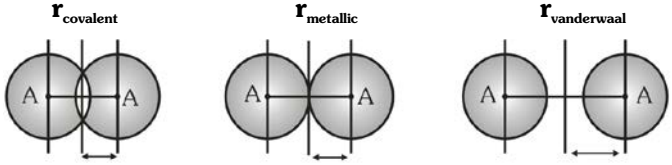
$Z_{eff} = Z - \sigma$



ATOMIC RADIUS

- Distance between centre of nucleus to outermost electron.
- Accurate value of atomic radius cannot be measured.
- We measure internuclear distance and assume half of it as atomic radii.
- On the basis of type of bond atomic radii is of following type :

Single bonded species



$r_{cov} = \frac{d_{A-A}}{2}$ $r_{metallic} = \frac{d_{A-A}}{2}$ $r_{vanderwaal's} = \frac{d_{A-A}}{2}$

Order of atomic radii of same atom

$r_{covalent} < r_{metallic} < r_{vanderwaal}$

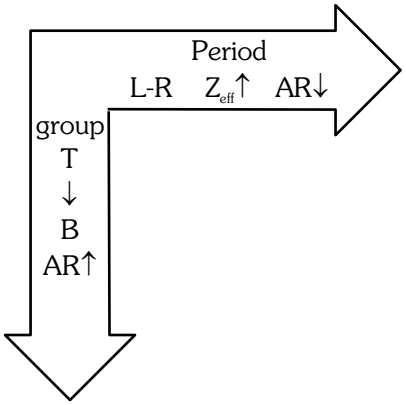
1 : 1.2 : 2

Factors of effecting atomic radii

$$\propto \frac{1}{Z_{eff}}$$

$$\propto \frac{1}{\text{bond strength}}$$

PERIODIC TRENDS



* Al ≃ Ga : Transition Contraction

* 4d ≃ 5d : Lanthanide Contraction

d-block p-block

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
^	≈	≈	≈	≈	≈	≈	≈	≈	≈	≈	≈
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb

Lanthanide contraction

La -->--> Lu 4f-series size↓

Eu → largest among 4f series

Ionic Radius

$A^+ \longleftarrow A \longrightarrow A^-$

Order of size : $A^+ < A < A^-$

Isoelectronic Species :

Same number of electrons

(a) same series species

$$\alpha - ve \propto \frac{1}{+ve}$$

$Na^+, Mg^{2+}, Al^{3+}, F^-, O^{2-}, N^{3-}$

$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$

(b) Different series (generally)

$2e^- < 10e^- < 18e^- < 36e^- < 54e^-$

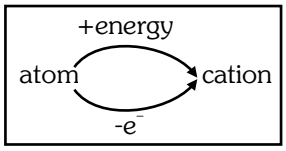
Eg. N^{3-} < Cs^+

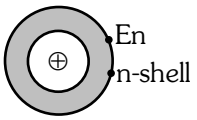
$10e^-$ $54e^-$

$F^- < Cl^- < H^-$

* Exceptional : $Li^+ \geq Mg^{2+}$

IONISATION ENERGY





DE = E∞–En
DE = IE = E∞–(–En)
IE = +ve Energy

Minimum amount of energy required to remove most loosely held electron from an isolated gaseous atom.

$M_{(g)} \xrightarrow{-e^-} M^+_{(g)} \quad \Delta H = +ve$

always an endothermic process

SUCCESSIVE IONISATION ENERGY

Energy required to remove successive electron from an atom known as successive ionisation energy.

$$M_{(g)} \xrightarrow[IE_1]{-e^-} M^+_{(g)} \xrightarrow[IE_2]{-e^-} M^{2+}_{(g)} \xrightarrow[IE_3]{-e^-} M^{3+}_{(g)}$$

(I) (II) (III)

Here : I e^-, II e^- & III e^- → successive e^-
&
IE_1, IE_2 & IE_3 → successive I.E.
Order of successive I.E. :
$IE_1 < IE_2 < IE_3$ always.
Total energy required for the formation of M^{n+} ion = $IE_1 + IE_2 + IE_3 + ...IE_n$

Factors & Periodicity

I.P

1. $\propto Z_{eff}$
2. $\propto \frac{1}{size}$
3. $\propto$ +ve charge
4. $\propto \frac{1}{-ve\ charge}$
5. e^- configuration : Stable configuration higher energy required. (only more than neighbor atom)
6. Penetration : s > p > d > f (applicable in neighbor atom)

Factor 5 & 6 applicable upto 4th period only
Be > B Sb < Te N > O

PERIODICITY

APPLICATION OF IP

Metallic character $\propto \frac{1}{IP}$

Reactivity of metal $\propto \frac{1}{IP}$

Electro+ve character $\propto \frac{1}{IP}$

Reducing naturer $\propto \frac{1}{IP}$

Period
L-R IP↑

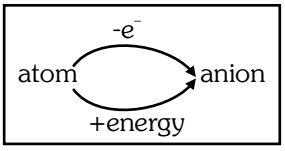
group
T
↓
B
IP↓

No. of valance e^- = consider successive IP
highest jump in successive IP indicate nobel gas configuration if it is 'a' then no. of valence e^-
valence e^- = a–1

STABILITY OF OXIDATION STATE

Consider successive IP
(a) If $\Delta IP \rightarrow$ < 11 eV higher o.s. stable
$\Delta IP \rightarrow$ > 16 eV lower o.s. stable

ELECTRON AFFINITY / ELECTRON GAIN ENTHALPY



Amount of energy released or absorb when an electron added to neutral gaseous atom.

$x_{(g)} + e^- \rightarrow x^-_{(g)}$

Generally Exothermic

If we measure energy in term of energy change it is known as electron gain enthalpy.

ΔH_{eg} = final state - initial state
(anion) (atom)

SUCCESSIVE ELECTRON AFFINITY

When an atom gain more than one e^-; these electrons are K/as successive electrons and their energy is K/as successive electron affinity.

I II

$x + e^- \xrightarrow{\text{energy}} x^- \xrightarrow{\text{energy}} x^{2-}$

$\downarrow \quad\quad \downarrow$

$EA_1 \quad EA_2$

EA_2 or higher always endothermic due to repulsion between anion & incoming electron.

FACTORS

E.A. $\propto Z_{eff}$ E.A. $\propto \frac{1}{\text{size}}$

Electron configuration :

Stable valence shell configuration of electron gaining would be a endothermic higher the stability of configuration higher endothermic process of electron gaining

order	Be $2s^2$	N $2s^2 2p^3$	Ne $2s^2 2p^6$
order of EA	Ne < Be < N max endo least endo		

PERIODICITY

$\rightarrow$EA$\uparrow$

ΔH_{eq} –ve$\uparrow$

$\downarrow$

EA$\downarrow$

ΔHeq

–ve

$\downarrow$

EXCEPTIONAL POINT

in p-block

EA of 2nd period < 3rd period

B	C	N	O	F	Maximum EA 'Cl'
^	^	^	^	^	O has least in
Al	Si	P	S	Cl	it's group.

ELECTRONEGATIVITITY

Tendency of an atom to attract shared pair of electron towards itself in bonded state is known as electronegativity.

$\rightarrow$ Relative Phenomenon.

$\rightarrow$ Unit less property.

$\rightarrow$ For Nobel gas we consider EN = zero.

Factors affecting **EN**:

1. $\propto Z_{eff}$
2. $\propto \frac{1}{\text{atomic size}}$
3. $\propto$ +ve o.s.
4. $\propto \frac{1}{\text{–ve o.s.}}$
5. $\propto$ %age of s-character

$sp > sp^2 > sp^3$

RELATIONSHIP BETWEEN IP & EA

$M \underset{+e^-;\ FA}{\overset{-e^-;\ IP}{\rightleftharpoons}} M^+ \qquad x \underset{-e^-;\ IP}{\overset{+e^-;\ EA}{\rightleftharpoons}} x^-$

PERIODIC TRENDS

Period

L-R EN$\uparrow$

group

T

$\downarrow$

B

EN$\downarrow$

Exception :

Zn < Cd < Hg

Ga < In < Tl

Application of Electronegativity

Bond & Bond properties

Non-polar bond $\Delta EN = 0$

Polar bond $\Delta EN \neq 0$

$\Delta EN\uparrow \rightarrow$ Bond polarity $\uparrow$ $\downarrow$ Bond length $\downarrow$ $\downarrow$ Bond strength $\uparrow$ $\downarrow$ Ionic character $\uparrow$

Bond length - Schoemaker stevenson formula = $d_{A-B} = r_A + r_B - 0.09 \times \Delta EN$

% age ionic character : Hanny -Smith formula = $16 \times \Delta EN + 3.5 (\Delta EN)^2$

Nature of Compounds

Oxides & hydroxides

- Acidic character $\propto$EN
- Basic character $\propto \frac{1}{EN}$

Electro negativity $\uparrow \rightarrow$ Acidic character of oxide $\uparrow$

Basic character of oxide $\downarrow$

Hydrides

- **s-block hydride** - Metallic hydride, basic character $\propto$ size
- **P-block hydride** - Non metallic hydride, acidic character $\propto$ size

IMPORTANT NOTE

CHAPTER 03

CHEMICAL BONDING

CHEMICAL BONDING

Force of attraction which holds two or more than two species together is known as bond.

H—H

H_2O :: H_2O Na^+ :: Cl^-

REASON

To attain the state of maximum stability, species have tendency of bonding.

CLASSIFICATION OF BONDS

On the basis of type of species getting bonded bonds can be classified into following categories.

BOND

- Interatomic bond between two atom strong bond 200 - 400 kJ/mol
  - Non-metal + Non-metal - covalent bond
  - Non-metal + Metal - Ionic bond
  - Metal + Metal - Metallic bond
  - ● Coordination bond is type of covalent bond
- Intermolecular force between molecules weak bond 2-40 kJ/mol
  - **H-bond**
  - 1. Ion-dipole
    2. Dipole-Dipole
    3. Ion-Induced dipole
    4. Dipole-Induced dipole
    5. London force

COVALENT BOND

Formation of covalent bond explained by three theories.

Lewis Octet Theory — **Valence Bond Theory** — **Molecular Orbital Theory**

LEWIS OCTET THEORY

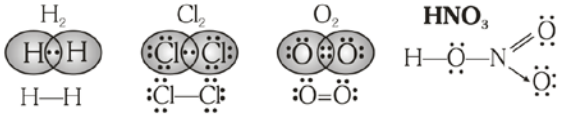
As per Lewis Octet Theory
Species do Bonding for Stability
Stability by achieving Nobel gas configuration.

VALENCE BOND THEORY

Atoms undergoes sharing of electron.
Sharing of electron leads to the formation of covalent bond.

VALENCE BOND THEORY

Sharing
- Equal sharing - Covalent Bond
- Unequal sharing- Coordinate Bond



EXCEPTION OF OCTET RULE

(a) electron deficient
Central atom:
No. of electron < 8
BeH_2
BF_3, BCl_3, BBr_3, BI_3
$AlCl_3$, $AlBr_3$, AlI_3

(b) electron rich
Central atom:
No. of electron > 8
PCl_5, IF_7
SF_6, XeF_2

(c) odd electron species
Central atom :
has odd electron
NO, NO_2, ClO_2
ClO_3

CO-ORDINATE BOND (DATIVE BOND)

In this type of bond, shared pair of electron donates by one species but shared by both

- For this type of sharing
- One species - must have lone pair - act as donar - known as Lewis base - acquire +ve charge.
- Another species - must have vacant orbital - act as acceptor - known as Lewis acid - acquire –ve charge.

Eg. $H_3N: + H^+ \rightarrow H_3N \rightarrow H^+$
LB LA

Similarly
$H_2O + H^+ \rightarrow H_3O^+$
$N_2H_4 + H^+ \rightarrow N_2H_5^+$
$AlCl_3 + AlCl_3 \rightarrow Al_2Cl_6$

- Donor atom follow octet rule

MODERN APPROACH OF COVALENT BOND

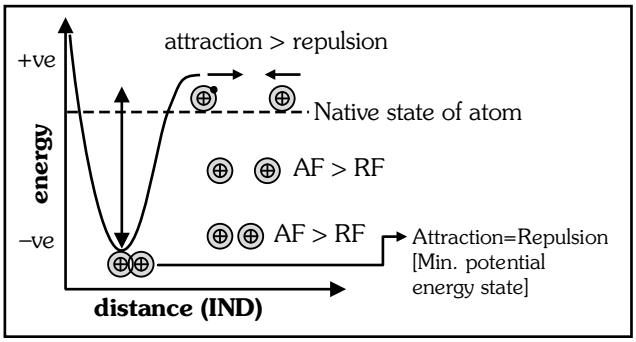
Consider wave mechanical model of atom means electron has dual nature; wave nature as well as particle nature considered by these theories, there are two theories in this approach.

1. Valence Bond Theory | **2. Molecular Orbital Theory**

Valence Bond Theory

Proposed by Heitler & London as per VBT bonding takes place for attaining stability.

$$\text{Stability} \propto \frac{1}{\text{Potential energy}}$$



- Bond formation is an exothermic process.
- During this process some extent of electron cloud merge into each other; this part is known as overlapped region & this process is known as overlapping.

Atom < Nucleus
Shell - subshell - orbital - electron - cloud

- Only those orbitals of valence shell can exhibit overlapping which has
- Unpaired electron

  For example
  H—Cl bond form by overlapping of 1s - 3p orbitals.
  $H \rightarrow 1s^1$
  $Cl \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^5$
- Opposite spin
- **Strength of Covalent Bond**

  Strength of covalent bond $\propto$ extent of overlapping.

  1. Nature of Orbitals

  (a) No. of shell : lower the number of shell, higher overlapping.

  $$\text{Bond Strength} \propto \frac{1}{\text{No. of shell}} / \text{size of orbitals}$$

  1-1 > 1-2 > 2-2 > 2-3

- Opposite $Cl_2 > Br_2 > F_2 > I_2$ due to
  O—O < S—S lp-lp
  N—N < P—P repulsion

(b) Type of Sub-shell
Valence shell contain subshell s & p

s-non-directional p-directional	Directional orbital has higher extent of overlapping

Possible combination & strength of overlapping

s-s < s-p < p-p

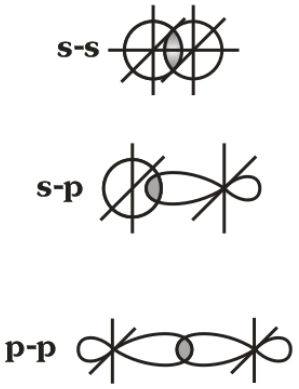
** This factor is applicable when number of shell is same otherwise shell factor prominent

2s - 2s < 2s-2p < 2p-2p sub-shell factor

1s - 1s > 1s-2s > 1s-3s shell factor

2. PATTERN OF OVERLAPPING

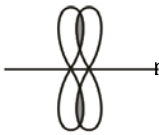
(a) Axial overlapping :
Along the internuclear axis; form sigma (s) bond, strong bond.



(b) Co-lateral overlapping
Side wise overlapping has less extent of overlapping form π-bond

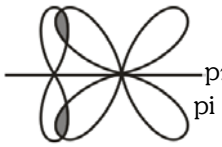
Weak bond

p-p overlapping



nternuclear axis
pπ-pπ
pi-bond

p-d overlapping



pπ-dπ
pi bond

According to VBT, In case of multiple bond between two atom one bond is sigma and rest are pi-bonds. VBT was not able to define geometry of molecule therefore a new concept came into existence known as hybridisation.

HYBRIDISATION

Intermixing of atomic orbitals and formation of new orbital, these orbitals are known as hybrid orbital and this concept is known as hybridisation.

It is hypothetical concept.

Only those orbitals can participate in hybridisation which has slight difference in energy.

No. of hybrid orbitals : No. of atomic orbitals participate in intermixing

Hybrid orbitals oriented at maximum possible distance three dimensionally.

Type of hybridisation.

S.No.	Type of orbital	No. of hybrid orbital	3D orientation	Example
1.	one s + one p	2; sp	Linear	BeH_2, $BeCl_2$
2.	one s + two p	3; sp^2	Triangular planer	BCl_3, BF_3
3.	one s + three p	4; sp^3	Tetrahedral	CH_4, CCl_4
4.	one s + three p + one d	5; sp^3d	Triangular bipyramidal	PCl_5
5.	one s + three p + two d	6; sp^3d^2	Octahedral/Square bipyramidal	SF_6
6.	one s + three p + three d	7; sp^3d^3	Pentagonal bipyramidal	IF_7

Valence Shell Electron pair repulsion theory

- Given by Nyholm & Gillespie to define shape of molecule.
- Shape of molecule define on the basis of electron pairs orientation present on central atom.
- Electron pairs present on central atom repel each other therefore these electron pair occupy such position on central atom; where they experience minimum repulsion at maximum possible distance three dimensionally.
- **Order of replusion :** lp-lp > lp-bp > bp-bp mb-mb > mb-sb > sb-sb

TYPE OF HYBRIDISATION & POSSIBLE STRUCTURE

Type of Hybridisation	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridisation	2	-	Linear	BeF_2, CO_2, CS_2, $BeCl_2$
2. (a) sp^2-hybridisation	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridisation	2	1	V-shape,Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridisation	4	0	Tetrahedral	CH_4, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-1}, SO_4^{-2}, $AlCl_4^-$
(b) sp^3-hybridisation	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+, PCl_3, XeO_3,$N(CH_3)_3$, CH_3^-
(c) sp^3-hybridisation	2	2	V-shape , Angular	H_2O, H_2S, NH_2^- , OF_2, Cl_2O, SF_2, I_3^+
4. (a)sp^3d-hybridisation	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_5
(b) sp^3d-hybridisation	4	1	See-Saw, folded square distorted tetrahedral	SF_4, PF_4^-, AsF_4^- SbF_4^-, XeO_2F_2
(c) sp^3d-hybridisation	3	2	almost T-shape	ClF_3, ICl_3
(d) sp^3d-hybridisation	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, ClF_2^-, XeF_2
5. (a) sp^3d^2-hybridisation	6	-	Square bipyramidal/octahedral	PCl_6^-, SF_6
(b) sp^3d^2-hybridisation	5	1	Square pyramidal	$XeOF_4$, ClF_5, SF_5^-, XeF_5^+
(c) sp^3d^2-hybridisation	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridisation	7	-	Pentagonal bipyramidal	IF_7
(b) sp3d3-hybridisation	6	1	distorted octahedral/apped octahedral	XeF_6
(c) sp3d3-hybridisation	5	2	Pentagonal planar	XeF_5^-

DIPOLE MOMENT

Measurement of Polarity in a molecule

$\boxed{\vec{\mu} = q \times d}$ debye = esu-cm

$1D = 10^{-18}$ esu.cm

(A) Identification of polar or Non-polar molecule.

Molecule : Symmetrical distribution of electron cloud- Non-polar.

Molecule : Unsymmetrical distribution of electron cloud- Polar.

Diatomic Molecule

(a) Homodiatomic $\Delta EN = 0 \rightarrow \vec{\mu} = 0 \rightarrow$ Non-polar

H_2, F_2, Cl_2, N_2 etc.

(b) Heterodiatomic $\Delta EN \neq 0 \rightarrow \vec{\mu}_{net} = 0 \rightarrow$ polar

HF > HCl > HBr > HI

Polyatomic molecule :

$\mu_R \rightarrow$ Vector sum of bond moment

$\mu_R \rightarrow \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$

Important Order

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

$NH_3 > SbH_3 > AsH_3 > PH_3$

$H_2O > H_2S$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$

$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

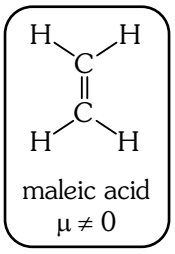
Applications

Predict shape and polarity of molecule

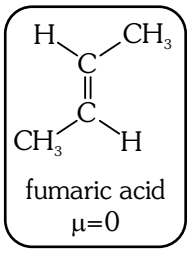
Symmetrical geometry $\rightarrow \mu = 0 \rightarrow$ non-polar

Unsymmetrical geometry $\rightarrow \mu \neq 0 \rightarrow$ polar

Distinguish between cis & trans form

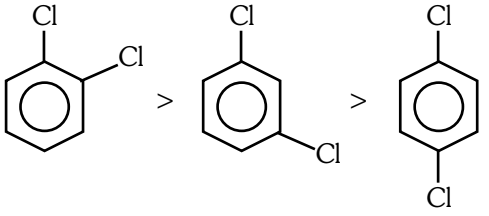


maleic acid
$\mu \neq 0$



fumaric acid
$\mu = 0$

Dipole moment in Aromatic Compounds



Orthodichloro benzene | metadichloro benzene | paradichloro benzene

$$\mu \propto \frac{1}{\text{bond angle}}$$

HYDROGEN BONDING

Electrostatic force of attraction between hydrogen & highly electronegative atoms.
It is dipole-dipole type of attraction
Hydrogen should be covalently bonded with highly electronegative elements. Like : F,O & N.
Strength of H-bond ∝ Electronegativity of electronegative elements

Type of Hydrogen Bond

- Intermolecular → Between molecule
- Intramolecular → Within molecule

- It is not an intermolecular force

EXAMPLES

- H_2O is liquid while H_2S is gas.
- HF is liquid while HCl is gas.
- Viscosity & Surface Tension: $\begin{matrix}CH_2–OH\\|\\CH–OH\\|\\CH_2OH\end{matrix} > \begin{matrix}CH_2–OH\\|\\CH_2–OH\end{matrix} > CH_3–OH$

Strength

Intermolecular H-bond > Intramolecular H-bond

- Intramolecular H-bonding takes place in ortho derivatives only.

Applications of H-bonding

Physical State	∝	H-bond
Melting Point (mp)	∝	H-bond
Boiling Point (bp)	∝	H-bond
Viscosity	∝	H-bond
Surface Tension	∝	H-bond
Volatility	∝	1/H-bond
Vapour Pressure	∝	1/H-bond

Specific Examples

- Solubility in H_2O : Any organic compound which get dissolve in H_2O, it is due to H-bonding.
- Association of Molecule : KHF_2 is possible but not $KHCl_2$ it is due to $K^+ [F^-$-----H–F] → ion dipole type h-bond

MOLECULAR ORBITAL THEORY

Given by Hund & Mulliken given

Given To explain :
- O_2 : Paramagnetic nature.
- Existence of species like H_2^+, H_2^-

As per MOT bond form by combination of atomic orbitals & interference of electron wave interference of electron wave leads to formation of molecular orbitals.

atomic orbitals - electron waves - interference < constructive interference / destructive interference

Constructive Interference → same phase wave - bonding molecular orbital (BMO)

Destructive Interference → opposite phase wave - anti-bonding molecular orbital (ABMO)

- Therefore by the combination of two atomic orbitals there is formation of two molecular orbitals; BMO & ABMO.
- Energy level BMO < ABMO.
- All atomic orbitals of an atom participate in combination and form molecular orbitals with atomic orbitals of another atom.
- Energy level of molecular orbital $\sigma 1s \;\; \sigma^*1s \;\; \sigma 2s \;\; \sigma^*2s \;\; \pi 2p_x = \pi 2p_y \;\; \sigma 2p_z \;\; \pi^*2p_x = \pi^*2p_y \;\; \sigma^*2p_z$

Total electron <14
Internuclear axis = z

SIGNIFICANT OF MOT

- Bonding electron (N_b) → No. of electrons present in BMO.
- Anti-bonding electron (N_a) → No. of electrons present in ABMO.
- **Bond order :** No. of Bonds present between two atoms.

$$B.O. = \frac{N_b - N_a}{2}$$

Stability of molecule ∝ B.O.

Bond strength ∝ B.O.

Bond length $\propto \frac{1}{B.O.}$

- **Paramagnetic nature :** If any molecule orbital contain unpaired electron, either bonding molecular orbital or anti-bonding molecular orbital it would be paramagnetic otherwise diamagnetic.
- **Isoelectronic species :** Same bond order - same magnetic properties.

Fractional bond order it will be always paramagnetic.

Sr. No.	No. of electrons in molecules	N_b	N_a	B.O.	Paramagnetic/ diamagnetic
1	1	1	0	½	paramagnetic
2	2	2	0	1	diamagnetic
3	3	2	1	0.5	paramagnetic
4	4	2	2	0	does not exist
5	5	3	2	½	paramagnetic
6	6	4	2	1	diamagnetic
7	7	4	3	½	paramagnetic
8	8	4	4	0	does not exist
9	9	5	4	½	paramagnetic
10	10	6	4	1	paramagnetic
11	11	7	4	1.5	paramagnetic
12	12	8	4	2	diamagnetic
13	13	9	4	2.5	paramagnetic
14	14	10	4	3	diamagnetic
15	15	10	5	2.5	paramagnetic
16	16	10	6	2	paramagnetic
17	17	10	7	1.5	paramagnetic
18	18	10	8	1	diamagnetic
19	19	10	9	0.5	paramagnetic
20	20	10	10	0	does not exist

In case of same bond order, stability depends upon

No. of anti-bonding electrons

$$\text{Stability} \propto \frac{1}{\text{No. of anti-bonding } e^-}$$

BONDING PARAMETER

1. Bond length : Internuclear distance
Factor affecting Bond length

(i) Atomic size : bond length ∝ size [No. of shell]

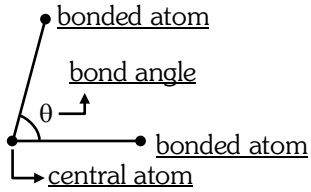
(ii) ΔEN, Bond length $\propto \frac{1}{\Delta EN}$

$$d_{A-B} = r_A + r_B - 0.09 \times \Delta EN \text{ (in Å)}$$

(iii) Bond order : Bond length $\propto \frac{1}{\text{B.O.}}$

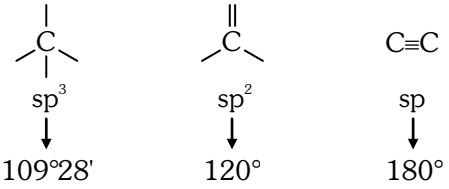
(iv) Hybridisation : Bond length $\propto \frac{1}{\text{\%age of s-character}}$

Bond Angle :
Angle between two adjacent bond is known as bond angle.



FACTORS AFFECTING BOND ANGLE

(i) Hybridisation
Bond angle ∝ %age of s-character



(ii) No. of lp/bp
[when hybridisation is same]
Bond angle $\propto \frac{1}{lp}$ Eg. : $CH_4 > NH_3 > H_2O$

(iii) Type of Central atom: Applicable when :
*hybridisation same *No. of lp/bp same
Bond angle μ EN of central atom
Eg. $NH_3 > PH_3 > AsH_3 > SbH_3$

(iv) Type of bonded atom : Applicable when
* hybridisation - same
* No. of lp/bp - same
* Central atom - same
Bond angle ∝ size of bonded species
Eg. $OF_2 < OCl_2 < OBr_2 < OI_2$

Note :
Regular geometry/same hybridisation/ bond angle same
$BF_3 = BCl_3 = BBr_3 = BI_3$

Ionic Bond

Extreme polar covalent bond is an Ionic Bond.
Therefore Ionic Bond ΔEN - Must be higher
one specie - lower EN - metal
one specie - higher EN - non metal
Eg. NaCl, KF
Formation of Ionic Bond takes place in following step.

$$\text{Metal (M) Solid} \xrightarrow[\Delta H = +ve,\ \text{S.E.}]{\text{Sublimation}} M(g) \xrightarrow[\Delta H = +ve,\ \text{I.E.}]{\text{Ionisation}} M^+_{(g)};\quad \underset{\text{Non metal molecule}}{X_2} \xrightarrow[\Delta H = +ve,\ \text{B.D.E.}]{\text{Dissociation}} X \xrightarrow[\Delta H = -ve,\ \text{electron gain enthalpy}]{+e^-} X^-_{(g)}$$

$$M^+_{(g)} + X^-_{(g)} \xrightarrow[\Delta H = -ve,\ \text{lattice energy}]{} MX_{(solid)}$$

$\Delta H_{formation}$ = S.E. + I.E. + ½ BDE + ΔH_{eg} + U
bond formation is always an exothermic process.
$\Delta H_{formation}$ = –ve

S.E. : should be lower
I.E. : should be lower
B.D.E. : should be lower
ΔHeg : should be higher
U : should be higher

Properties of Ionic Salt

General Properties :

Hard, Solid, Brittle (strong electrostatic attraction between ions)

Non directional nature (ionic compound do not exhibit stereo isomerism)

Higher Melting Point / Boiling Point

Isomorphism : $MgSO_4.7H_2O$; $ZnSO_4.7H_2O$; $FeSO_4.7H_2O$

Specific Properties

Conduction | Solubility | Covalent Character

Molten state

Ionic conduction $\propto \frac{1}{\text{Ionic radius}}$

Eg. : LiCl, NaCl, KCl, RbCl, CsCl

Ionic Radius : $Li^+ <<< Cs^+$

Conductance : CsCl < RbCl < KCl < NaCl < LiCl

Aqueous medium

Ionic mobility $\propto \frac{1}{\text{Ionic radius}}$

Hyd. radius : $Cs^+ <<< Li^+(aq)$

conductance : LiCl < NaCl < KCl < RbCl < CsCl

COVALENT CHARACTER / FAJAN'S RULE

Ionic potential of cation(ϕ) $\propto \frac{\text{charge of cation}}{\text{size of cation}}$

Polarisibility of anion ∝ size of anion ∝ charge of anion

Condition for polarisation
- Smaller cation
- Large anion
- Higher charge

FACTORS AFFECTING POLARISATION

(1) Polarisation $\propto$ charge of cation or anion

Eg.

(i) $\overset{+2}{CrO} < \overset{+3}{Cr_2O_3} < \overset{+6}{CrO_3}$ Covalent character ↑

(ii) $\overset{+2}{SF_2} < \overset{+4}{SF_4} < \overset{+6}{SF_6}$ Covalent character ↑

(iii) $\overset{-1}{LiF} < \overset{-2}{Li_2O} < \overset{-3}{Li_3N}$ Covalent character ↑ (anion charge↑)

(2) Polarisation $\propto \frac{\text{size of anion}}{\text{size of cation}}$

Eg.

(i) $LiF < LiCl < LiBr < LiI$ — anion size↑, polarisability↑, covalent character↑

(ii) $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$ — cation size↑, polarisation↓, covalent character↓

IMPORTANT NOTE

CHAPTER 04

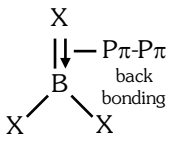
p-BLOCK ELEMENTS

BACK BONDING

Back bonding : Coordinate type π bond.
If coordinate type π bond get form between central atom & bonded atom of a molecule it is known as back bonding.

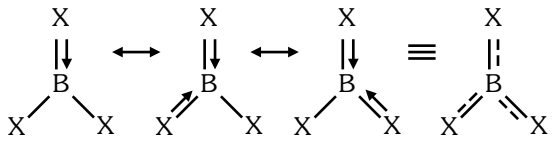
Condition for formation of back bonding
- One species must have lone pair.
- another species must have vacant orbital.
- size of atom should be small.

Eg. 1 Back bonding in Boron Trihalide



X=F, Cl, Br, I
X → Contain lp -------donar
B → Contain vacant orbital - acceptor

Eg. 2 Exhibit resonance in Back bond

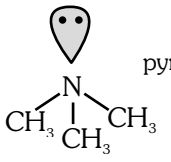


Extent of back bonding $BF_3 > BCl_3 > BBr_3 > BI_3$
(2p-2p, 2p-3p, 2p-4p, 2p-5p)

Lewis acid strength $BF_3 < BCl_3 < BBr_3 < BI_3$

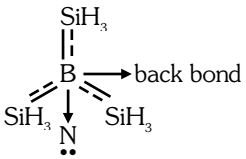
Few more examples of back bonding

1. Shape of trimethyl amine pyramidal while shape of trisillyl amine is triangular planar.



pyramidal

No back bonding due to no vacant orbital in carbon.



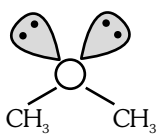
Trigonal Planar

2. Lewis base strength

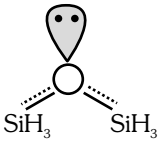
$\ddot{N}(CH_3)_3 > \ddot{N}(SiH_3)_3$

lp involve in back bonding

3. Bond angle of $(CH_3)_2O$ is very less than $(SiH_3)_2O$



No back bonding
C : No vacant orbital



back bond effect of lp↓
bond angle↑

INERT PAIR EFFECT

Some heavy metallic elements of P-block exhibit higher stability in lower oxidation state in comparisons of their group oxidation state it is due to inert pair effect.

$Tl^{+1} > Tl^{+3}$
$Pb^{+2} > Pb^{+4}$
$Bi^{+3} > Bi^{+5}$

electron pair of s-subshell of valence shell is reluctant to participate during chemical combination, it is known as inert pair & this effect is known as inert pair effect.

It is due to higher amount of energy required for this electron pair removal which is not compensated by bond formation energy.

Generally in oxide & fluorides inert pair effect becomes non-effective [due to higher bond energy]

$TlCl$ exist but not $TlCl_3$
PbI_2 exist but not PbI_4
$BiCl_3$ exist but not $BiCl_5$
due to inert pair effect

Order of stability of oxidation state

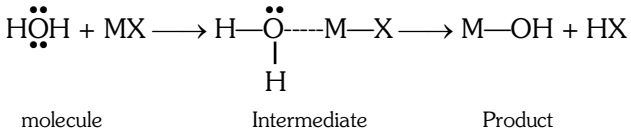
$B^{+3} > Al^{+3} > Ga^{+3} > In^{+3} > Tl^{+3}$

$B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$

$C^{2+} < Si^{2+} < Ge^{2+} < Sn^{2+} < Pb^{2+}$

HYDROLYSIS
Hydro - Water
lysis - break down

Break down of a molecule through water and formation of new product is known as hydrolysis.

- It is nucleophilic substitution reaction.
- 

molecule Intermediate Product

Extent of hydrolysis ∝ covalent character.

$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$

$BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$

$AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$
$SiCl_4 + 4HOH \rightarrow Si(OH)_4 + 4HCl$
or SiO_2

$SF_6 + H_2O \rightarrow$ No hydrolysis due to crowding

$CCl_4 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

Carbon → No vacant orbital.

$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$

$3BF_3 + 3HF \rightarrow 3H^+ [BF_4]^-$

$4BF_3 + 3H_2O \rightarrow 3H[BF_4]$
(partially hydrolysis)

15th Group Halides

$NF_3 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis

$NCl_3 + HOH \longrightarrow NH_3 + 3HOCl$

$PCl_3 + HOH \longrightarrow H_3PO_3 + 3HCl$

$AsCl_3 + HOH \longrightarrow As(OH)_3 + 3HCl$

$SbCl_3 + HOH \longrightarrow SbOCl + 2HCl$
(partial hydrolysis)

$BiCl_3 + HOH \longrightarrow BiOCl + 2HCl$
(partial hydrolysis)

$PCl_5 + HOH \longrightarrow POCl_3 \rightarrow H_3PO_4$
partial completely

Hydrolysis of higher covalent character containing salt

$Be_2C + 4HOH \longrightarrow 2Be(OH)_2 + CH_4$

$Mg_2C_3 + 4HOH \longrightarrow 2Mg(OH)_2 + C_3H_4$

$CaC_2 + 2HOH \longrightarrow Ca(OH)_2 + C_2H_2$

$Al_4C_3 + 12HOH \longrightarrow 4Al(OH)_3 + 3CH_4$

$Mg_3N_2 + 6HOH \longrightarrow 3Mg(OH)_2 + 2NH_3$

$AlN + 3HOH \longrightarrow Al(OH)_3 + NH_3$

$Ca_3P_2 + 6HOH \longrightarrow 3Ca(OH)_2 + 2PH_3$

$LiH + HOH \longrightarrow LiOH + H_2$

$CaH_2 + 2HOH \longrightarrow Ca(OH)_2 + H_2$

Hydrolysis of Interhalogen Compounds

$AX + HOH \longrightarrow HX + HOA$

$AX_3 + HOH \longrightarrow 3HX + HAO_2$

$AX_5 + HOH \longrightarrow 5HX + HAO_3$

$AX_7 + HOH \longrightarrow 7HX + HAO_4$

HX Hydrohalic acid
HOA, HAO_2, HAO_3 HAO_4
oxyacid of halogen

OXY-ACIDS

- Mainly oxy-acids are hydroxide of Non-metal oxides.
- No. of H^+ ion furnish by an oxyacid is known as their basicity.
  Oxyacid obtained by dissolving non-metal oxide in water.
  Eg. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$
  Here : $CO_2 \rightarrow$ Non metal oxide - Anhydride of carbonic acid
  $OC(OH)_2 \rightarrow$ Oxyacid
- $NO_2 \longrightarrow$ Mixed anhydride
- it gives $\longrightarrow HNO_2$ & HNO_3

Oxide Acid

- $N_2O_3 \longrightarrow HNO_2$ — Nitrous acid
- $N_2O_5 \longrightarrow HNO_3$ — Nitric acid
- $P_4O_{10} \longrightarrow H_3PO_4$ — Phosphoric acid
- $SO_2 \longrightarrow H_2SO_3$ — Sulphurous acid
- $SO_3 \longrightarrow H_2SO_4$ — Sulphuric acid
- $Cl_2O_7 \longrightarrow HClO_4$ — Perchloric acid
- Oxyacids of different elements

	Element	Oxide	Oxyacid	Basicity
1	Boron	B_2O_3	$B(OH)_3$ boric acid	Not protonic acid monobasic Lewis acid
2	Carbon	CO_2	H_2CO_3 carbonic acid	Two
3	Nitrogen		$H_2N_2O_2$ Hyponitrous acid HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid	
4	Phosphorus		H_3PO_2 Hypophosphorus acid H_3PO_3 Phosphorus acid H_3PO_4 Ortho phosphoric acid HPO_3 Meta phosphoric acid $H_4P_2O_5$ Pyrophosphorus acid $H_4P_2O_7$ Pyrophosphoric acid $H_4P_2O_6$ Hypophosphoric acid	

Order of acidic strength
$H_3PO_2 > H_3PO_3 > H_3PO_4$
Reducing nature
$H_3PO_2 > H_3PO_3 > H_3PO_4$

OXYACIDS OF SULPHUR

1. Sulphurous acid - H_2SO_3
2. Sulphuric acid - H_2SO_4
3. Thiosulphuric acid - $H_2S_2O_3$
4. Peroxymonosulphuric (Caro's acid) - H_2SO_5 (Peroxide bond)
5. Peroxydisulphuric acid (Marshal's acid)-$H_2S_2O_8$ (Peroxide bond)
6. Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
7. Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
8. Thionus acid - $H_2S_2O_4$
9. Thionic acid - $H_2S_2O_6$
10. Polythionus acid - $H_2(S)_nO_4$ (S-S linkage)
11. Polythionic acid - $H_2(S)_nO_6$ (S-S linkage)

OXYACIDS OF HALOGEN (Cl)

1. Hypochlorous acid- HClO
2. Chlorous acid - $HClO_2$
3. Chloric acid - $HClO_3$
4. Perchloric acid - $HClO_4$

Order of acidic strength
$HClO < HClO_2 < HClO_3 < HClO_4$

Oxidising nature
$HClO > HClO_2 > HClO_3 > HClO_4$

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

ALLOTROPES OF CARBON

DIAMOND

$C\text{-}sp^3$, tetrahedral structure
C-C bond length 1.54 Å
Compact 3 dimensional structure
Hardest substance
Very high mp (~ 3400°C)
Very high density
Non conductor
Very high refractive index
Exhibit total internal reflection
Shines brighty in light

GRAPHITE

Hexagonal layer structure
All sp^2 hybrid carbon
Unhybrid orbital electron form π-bond.
This π-bond exhibit resonance and due to resonance there is mobility of electrons and it becomes conductor of electricity.

FULLERENE

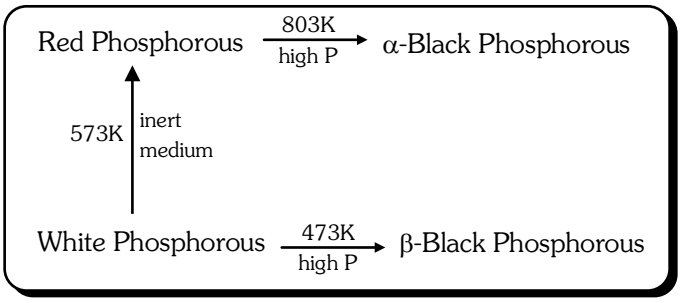
Latest discovered allotrope of carbon it is found in chimney sooty particle.
It contain C_{60}-C_{320}; C : sp^2 hybrid
Contain pentagonal & hexagonal structure
C_{60}:Buckminster fullerene soccer ball (football) or bucky ball.
C_{60} : 20 hexagon rings
12 pentagon rings
Purest form of carbon
No dangling bond

ALLOTROPES OF PHOSPHOROUS

(a) white phosphorous (b) Red phosphorous (c) Black phosphorous

White phosphorous	**Red Phosphorous**
Waxy solid	Brittle powder
Poisonous	Non poisonous
Soluble in CS_2, Insoluble in water	Insoluble in water & CS_2
Monomer of P_4	Polymer of P_4
Highly reactive due to bond angle strain	More stable than white phosphorous
It glows in dark due to slow oxidation (phosphorescence)	It does not glow in dark
It gives phosphine (PH_3) on reaction with NaOH	It gives hypo phosphoric acid on reaction with NaOH

Order of stability or MP or density → white < red < black



ALLOTROPES OF SULPHUR

S

Crystalline

Rhombic sulphur (α-S)
most stable form

Monoclinic sulphur (β-S)

$\alpha - S \underset{<95^\circ,6^\circ C}{\overset{>95.6^\circ C}{\rightleftharpoons}} \beta - S$

95.6℃ = transition Temp.
both are soluble in CS_2
but insoluble in water

Amorphous

Milk of sulphur
Plastic sulphur (γ-S)

Colloidal sulphur

$\underset{RA}{H_2S} + 2\underset{OA}{HNO_3} \xrightarrow[Redox]{} S + 2NO_2 + 2H_2O$

(a) density of αS > βS
(b) Both are puckered crown shape having S_8 units
(c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.
(d) S_6 is chair form of S

Effect of Temperature

$S_{8(\alpha)} \xrightarrow{95.5^\circ C} S_{8(\beta)} \xrightarrow{119^\circ C} S_{(liq)} \xrightarrow{130\text{-}200^\circ C}$ Viscosity of liquid increase $\xrightarrow{> 200^\circ C}$ Viscosity decrease

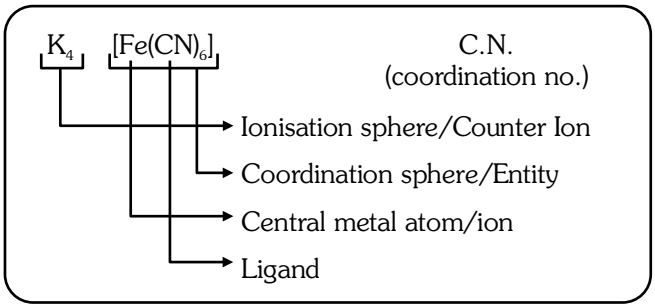
IMPORTANT NOTE

CHAPTER 05

COORDINATION CHEMISTRY

COMPLEX COMPOUND

Representation of coordination compound



LIGANDS

Species which donate lone pair/electron pair is called as ligand, on the basis of the number of e pairs available for donation; ligands are classified as

LIGANDS

- On the basis of charge
  - → Neutral
  - → Anionic
  - → Cationic
- On the basis of denticity
  - → Monodentate
  - → Bidentate
  - → Polydentate
  - → Flexidentate
  - → Ambidentate
- On the basis of lp donation/accepting e^- s
  - Classical
  - Non-classical
    - π e^- donating ligand
    - π acid ligand

On the basis of denticity

Monodentate : have only one donor sites. Eg. H_2O, NH_3

Bidentate : Contain two donor sites. Eg. $CH_2=CH_2$, $\begin{matrix}COO^-\\|\\COO^-\end{matrix}$

AMBIDENTATE LIGAND

They can change their donor atom (side) but not denticity.

Eg. :

$-CN^-$, and $-NC^-$, $-SCN^-$ and $-NCS^-$, NO_2^- and ONO^-, $-OCN^-$ and NCO^-.

These ligands are responsible for linkage isomerism.

CHELATING LIGAND

These are the polydentate ligands which bind to the central metal to form a ring structure. Chelation leads to extra stability, for example, EDTA (ethylene diamine tetra acetate).

FLEXIDENTATE LIGANDS

Exhibit variable denticity. Eg. SO_4^{2-}, CO_3^{2-}, $EDTA^{4-}$

BONDING IN COORDINATION CHEMISTRY

BONDING

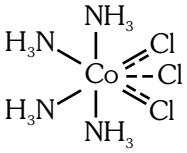
Werner Theory | Valence Bond Theory | Crystal Field Theory

WERNER'S THEORY

Metal in a complex shows two type of valences - Primary & secondary.

Primary Valency	Secondary Valency
It is oxidation no. of metal.	It is coordination number
It is variable	It is non variable.
Satisfied by anions (present in coordination or ionisable sphere).	Satisfied by ligands (present in coordination sphere)
Ionisable	Non ionisable
Ionic ∴ nondirectional	Directional ∴ decide geometry of complex ion.
Represented by dotted line in Werner structure.	Represented by solid lines in Werner structure.

Eg. $COCl_3.4NH_3$ (Molecular formula) $[Co(NH_3)_4Cl_2]Cl$ (Complex formula)



Werner structure

{3 dotted line shows - Primary Valence
6 solid line shows - Secondary Valence

VALENCE BOND THEORY

Central metal atom/ion & ligand come close to each other ligand donate lone pair & CMA provide vacant orbital.

There is hybridisation of atomic orbitals provided by central atom to ligands.

Type of Orbitals participating in intermixing depend upon two factors.

(a) Availability of orbitals (b) Nature of ligand

Coorination No.	Type of hybrid orbital
2	sp
3	sp^2
4	square planar -dsp^2 / tetrahedral -sp^3
5	dsp^3 / sp^3d
6	sp^3d^2 - outer orbital complex (high spin) / d^2sp^3 - inner orbital complex (low spin)

Eg. :

$[NiCl_4]^{2-}$ sp^3 ----- Tetrahedral
$[Ni(CN)_4]^{2-}$ dsp^2 ----- Square planar
$[Ni(CO)_4]$ sp^3 ----- Tetrahedral
$[Zn(NH_3)_4]^{2+}$ sp^3 ----- Tetrahedral
$[Cu(NH_3)_4]^{2+}$ dsp^2 ----- Square planar

Coordination No. 6 : Example

$[Fe(CN)_6]^{4-} \rightarrow d^2sp^3$
$[Fe(CN)_6]^{3-} \rightarrow d^2sp^3$
$[Co(NH_3)_6]^{3+} \rightarrow d^2sp^3$
$[Ni(H_2O)_6]^{2+} \rightarrow sp^3d^2$

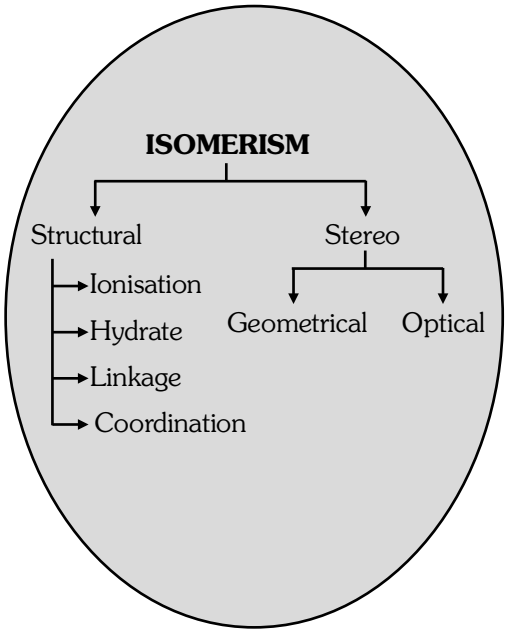
VALENCE BOND THEORY

- If the complex is formed by the use of inner d-orbitals for hybridisation (d^2sp^3), it is called inner orbital complex.
- If the complex is formed by the use of outer d-orbitals for hybridisation (sp^3d^2), it is called an outer orbital complex. Such a complex is also called as high spin complex e.g. $[CoF_6]^{3-}$.

CRYSTAL FIELD THEORY (CFT)

CRYSTAL FIELD SPLITTING

- The splitting of five degenerate d-orbitals of the metal into different sets of orbitals having different energies in the presence of electrostatic field of ligands is called crystal field splitting.
  $e_g$set – $dx^2–y^2$, dz^2 t_{2g} set–dxy, dyz, dxz
- Crystal field splitting energy, (D_O for octahedral structure and $\Delta_t = 4/9\Delta_0$ tetrahedral structure) is the difference between the various sets of energy levels formed by crystal field splitting.
- Weak field ligands are those ligands which cause a small degree of crystal field splitting
  e.g. I^-, Br^-, Cl^-, F^-, OH^-, $C_2O_4^{2-}$, H_2O, etc.
- Strong field ligands are those ligands which cause a high degree of splitting e.g. CO, CN^-, NO^{2-}, etc.
- Spectrochemical series
  $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < ox^{2-} < H_2O <$ py ~ en < dipy < o-phen < $NO_2^- < CN^- <$ CO.
  (C and N donar act as SFL except N_3^-)
- For 4d & 5d element all ligands acts as S.F.L.
- With CO^{+3} $(OX)^{-2}$, H_2O acts as S.F.L.
- With Fe^{+2} & Mn^{+2}, NH_3 act as W.F.L.



Important Point :

	Extent of synergic bonding	M–C B.L.	C–O B.L.
$[M(CO)_n]^-$	Max.	Min.	Max.
$[M(CO)_n]^+$	Min.	Max.	Min.

STRUCTURAL

(a) Ionisation isomerism : Same molecular formula but gives different ionisable species. (Only anionic)

$PtCl_2Br_2.4NH_3$ → (a) $[Pt(NH_4)_4Cl_2]Br_2$; (b) $[Pt(NH_3)_4Br_2]Cl_2$

(b) Hydrate isomerism : Same molecular formula but different number of water molecules associated with central metal.

$CrCl_3.6H_2O$ → (a) $[Cr(H_2O)_6]Cl_3$; (b) $[Cr(H_2O)_5Cl]Cl_2.H_2O$; (c) $Cr(H_2O)_4Cl_2]Cl.2H_2O$

(c) Linkage isomerism : Structural isomerism shown by ambidentable ligands

$(NO_2^-,\ SCN^-,\ CN^-,\ OCN^-$ etc.)

$[Fe(NH_3)_5(SCN)]^{2+}$ $[Fe(NH_3)_5(NCS)]^{2+}$

(d) Coordination isomerism : Isomers having both anion and cation as complex entity. Can inter change position of ligands as well as metal.

$[Cr(NH_3)_6][Co(CN)_6]$ $[Co(NH_3)_6][Cr(CN)_6]$

STEREOISOMERISM

(a) Geometrical Isomerism (GI)

CN = 4

Tetrahedral (No G.I.)

Squre planar

- Ma_4 – NO GI
- Ma_3b – NO GI
- Ma_2b_2 – 2 GI (cis & trans)
- Ma_2bc – 2 GI (cis & trans)
- Mabcd – 3 GI

CN = 6 (Octahedral)

- Mabcdef – 15 GI
- Ma_2bcde – 9 GI
- Ma_2b_2cd – 6 GI
- $Ma_2b_2c_2$ – 5 GI
- Ma_3bcd – 4 GI
- Ma_3b_2c – 3 GI
- Ma_3b_3 – 2(Fac-Mer)
- Ma_4bc – 2(cis-trans)
- Ma_4b_2 – 2(cis-trans)
- Ma_5b – NO GI
- Ma_6 – NO GI

Sq. planar complex with symmetrical bidentate ligand. Eg. No GI

Sq. planar complex can exhibit GI only in two types [$M(AB)_2$, M(AB)(CD)]

* On increasing number of one type of ligand total number of geometrical isomers decreases.

Whenever same type of ligand placed at 180° it will not show O.I.

$[M(AA)_2a_2]$ type of complex have two GI (cis & trans)

* $[M(AA)_2a_2]$ type of complex gives three stereo isomer :
(1) cis (2) trans (3) mirror image of cis

ORGANOMETALLIC COMPOUDS

Compounds in which the less E.N. (Ge, Sb, B, Si, P, As) central metal atoms are bonded directly to carbon atoms are called organometallic compounds.

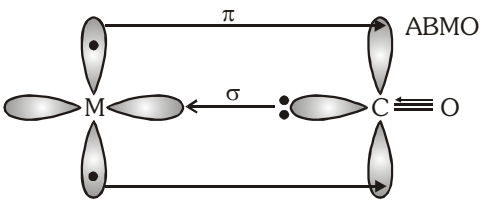
- **σ-bonded compounds** formed by nontransition elements.

  R–Mg–X, $(CH_3–CH_2)_2Zn$, Ziegler natta catalyst, etc.

- **π-bonded organometallic compounds** are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzene chromium, etc.

- **σ-and π-bonded organometallic compounds :** Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.

Synergic bonding



IUPAC NOMENCLATURE OF COMPLEX COMPOUNDS :

(A) For anionic complex (like $K_4[Fe(CN)_6]$)
Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + Ox. St (in roman number).
eg. : Potassium hexacyanoferrate (II)

(B) For cationic comlex like $[Cu(NH_3)_4]SO_4$
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St (In roman number) + Name of anion (without numeral prefix)
eg. : Tetraammine copper (II) sulphate.

(C) For neutral complex (like $[Fe(CO)_5]$)
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St. (In roman number)
eg. : Pentacarbonyl iron (O)

(D) Rule same just apply alphabetical order when write the name of ligands.
e.g. $[Pt(NH_3)_2Cl_2]$
Diamminedichloroplatinum (II)

IMPORTANT NOTE

CHAPTER 06

d-BLOCK (Transition Elements)

DEFINITION

Incomplete n and n–1 shell in atomic or in ionic state. Zn, Cd & Hg – are d-block nontransition elements.

GENERAL ELECTRONIC CONFIGURATION

$$ns^{0-2}\ (n-1)d^{1-10}$$

$$\text{Exceptions}\begin{cases} Cr = 4s^1\ 3d^5 \\ Cu = 4s^1\ 3d^{10} \end{cases},\ Pd = 5s^0 4d^{10}$$

TRANSITION SERIES

1st	3d series	Sc_{21} — Zn_{30}	9 + 1 = 10
2nd	4d series	Y_{39} — Cd_{48}	9 + 1 = 10
3rd	5d series	La_{57}, Hf_{72} — Hg_{80}	9 + 1 = 10
4th	6d series	Ac_{89}, Unq_{104} — Uub_{112}	9 + 1 = 10

ATOMIC RADIUS

3d series Sc > Ti > V > Cr > Mn ≥ Fe ≃ CO ≃ Ni ≤ Cu < Zn

In a group 3d to 4d series increases but 4d and 5d series nearly same due to poor shielding of f electron. (Lanthanide contraction)

$$\boxed{3d < 4d \simeq 5d}$$

e.g. Ti < Zr ≃ Hf $\begin{vmatrix} \text{Smallest radius} - \text{Ni} \\ \text{Largest radius} - \text{La} \end{vmatrix}$

Melting point : s-block metals < d-block metals

In a series on increasing number of unpaired e^- mpt increases upto Cr then decreases.

Sc < Ti < V < Cr > Mn < Fe > Co > Ni > Cu > Zn

↓ Half filled d^5 ∴ weak metallic bond ; ↓ Fully filled d^{10} ∴ weak metallic bond

Melting point $\begin{vmatrix} Zn > Cd > Hg \\ Cu > Ag \le Au \end{vmatrix}$ (data based)

E.N. Exception Zn < Cd < Hg

Density : s-block metals < d-block metals.

3d series

Sc < Ti < V < Cr < Mn < Fe < Co ≤ Ni < Cu > Zn

Density in a Group 3d < 4d << 5d

Metallic character : They are solid, hard, ductile, malleable, good conductor of heat and electricity and exhibit metallic lusture, high tensile strength. Hg is liquid

Elect. cond. $\underbrace{Ag > Cu > Au}_{d-block} > \underset{p-block}{Al}$

OXIDATION STATE

Transition elements exhibit variable oxidation state due to small energy difference of ns and (n–1)d electrons.

- Sc(+3) and Zn(+2) exhibit only one oxidation state
- Common oxidation state is +2
- 3d series highest oxidation state is +7 (Mn)
- In d-block series highest oxidation state is +8 (Os, Ru)
- In carbonyl compound oxidation state of metals is zero due to synergic effects.
- Their higher oxidation states are more stable in fluoride and oxides.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.
  eg. stable fluoride in higher oxidation state of Mn is MnF_4 while oxide is Mn_2O_7

Some more stable oxidation states of d-block elements			
Cu +2	Mn +2	Pt +4	Ag +1
Cr +3	Sc +3	Au +3	Ni +2

Common oxidation states			
Ti(+4),	V(+5)	Cr(+3,+6)	Mn(+2,+4,+7)
Fe(+2, +3),	Co(+2,+3)	Ni (+2)	Pt (+2+4)

In p-block lower oxidation states of heavier elements are more stable while in d-block heavier element, higher oxidation state are more stable.
eg. In VIB gp Mo(+6) & W(+6) are more stable than Cr(+6)

MAGNETIC PROPERTY

All transition elements are paramagnetic due to presence of unpaired electrons. They attract when magnetic field is applied. Magnetic moment of unpaired electron is due to spin and orbital angular momentum.

"Spin only" magnetic moment can be calculated by using formula $\mu = \sqrt{n(n+2)}$ Bohr magneton. (n is number of unpaired e^-.)

If n is 1 μ = 1.73 BM n is 2 μ = 2.84 BM n is 3 μ = 3.87 BM

n is 4 μ = 4.90 BM n is 5 μ = 5.92 BM

Substances that are not attracted by applied magnetic field are diamagnetic. They have all the electrons paired. d-block element and ions having d^0 and d^{10} configuration are diamagnetic.

COLOUR

Colour in transition metal ions is associated with d–d transition of unpaired electron from t_{2g} to e_g set of energies.

This is achieved by absorption of light in the visible spectrum, rest of the light is no longer white.

Colourless – Sc^{3+}, Ti^{4+}, Zn^{2+} etc

Coloured – Fe^{3+} yellow , Fe^{2+} green, Cu^{2+} blue, Co^{3+} blue etc.

Interstitial compounds : When less reactive nonmetals of small atomic size eg. H, B, N, C, Trapped in the interstitial space of transition metals, interstitial compounds are formed, like :- TiC, Mn_4N, Fe_3H etc.

They are nonstoichiometric compounds. They have high melting point than metals. They are chemically inert.

ALLOYS

Solid mixture of metals in a definate ratio

(15% difference in metallic radius)

They are hard and having high melting point.

eg. Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mix with other metals form semisolid amalgam except Fe,Co,Ni, Li.

CATALYST

Transition metals & their compounds act as catalyst due to –

– Variable oxidation state

– Tendency to form complex

eg. V_2O_5 – Contact process

Fe – Haber process

Ni – Catalytic hydrogenation

IMPORTANT REACTIONS OF d-BLOCK ELEMENTS

(a) $Cu^{2+} + 4I^- \longrightarrow Cu_2I_{2(s)} + I_2$

(b) $CuSO_4 + \underset{\text{Excess}}{KCN} \longrightarrow K_2SO_4 + \underset{\text{Unstable}}{Cu(CN)_2}$

$2Cu(CN)_2 \longrightarrow 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$

$CuCN + 3KCN \longrightarrow K_3[Cu(CN)_4]$

(c) $Cu \xrightarrow[\text{moist air}]{H_2O+CO_2} \underset{\text{green}}{CuCO_3.Cu(OH)_2}$

$Au \xrightarrow[(3HCl+HNO_3)]{\text{Aqua regia}} H[AuCl_4] + NOCl + H_2O$

(d) $AgNO_3 \xrightarrow{\text{Heating}} Ag + NO_2 + \frac{1}{2}O_2$

$AgCO_3 \xrightarrow{\text{Heating}} Ag + CO_2 + \frac{1}{2}O_2$

(e) $CuSO_4.5H_2O \xrightarrow{100^\circ C} \underset{\text{light greenish blue}}{CuSO_4.H_2O} \xrightarrow{230^\circ C} \underset{\text{Colourless}}{CuSO_4}$

$\xrightarrow{720^\circ C} CuO + SO_2 + \frac{1}{2}O_2$

(f) $Hg_2Cl_2 + NH_4OH \longrightarrow Hg\underset{\text{Cl}}{\overset{\text{NH}_2}{\diagup}}$ (Black)

(g) $NO_3^- / NO_2^- \xrightarrow{FeSO_4+H_2SO_4} \left[Fe(H_2O)_5NO^+\right]SO_4$

(h) $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Photographic complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$ (Brown ring complex)

COMPOUNDS OF d-BLOCK ELEMENT

A. $K_2Cr_2O_7$:

Method of preparation :

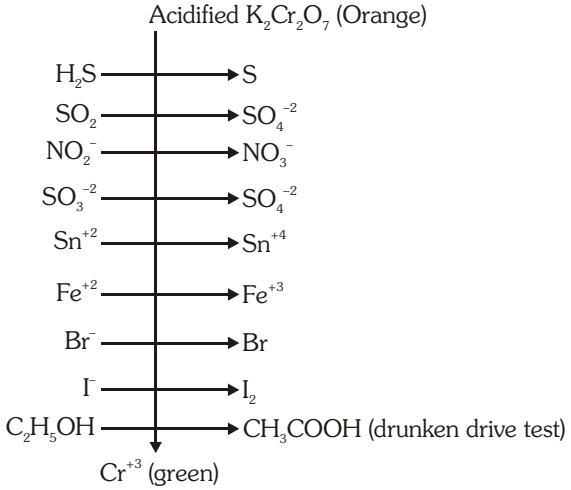
$$\underset{\text{(Chromite)}}{4FeO.Cr_2O_3} + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$\downarrow$$
$$K_2Cr_2O_7$$

Important point :

- $\underset{\text{Yellow}}{CrO_4^{-2}} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Orange}}{Cr_2O_7^{-2}}$
- $K_2Cr_2O_7$ used in volumetric analysis not $Na_2Cr_2O_7$.
- Hetaing effect $\rightarrow 2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$
- Chromyl chloride test $\rightarrow$ Used to detect ionic chloride (Cl^-)

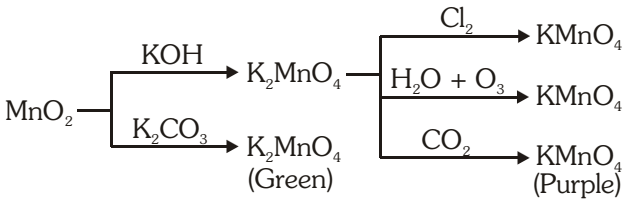
$$NaCl + K_2Cr_2O_7 + H_2SO_4 \longrightarrow CrO_2Cl_2 \text{ (Red orange)}$$

- With $H_2O_2 \rightarrow Cr_2O_7^{-2} + H^+ + 4H_2O_2 \longrightarrow CrO_5$ (Deep Blue sol.)
- Act as an oxidising agent.



B. $KMnO_4$:

Method of preparation :



Property :

- Effect of heating :

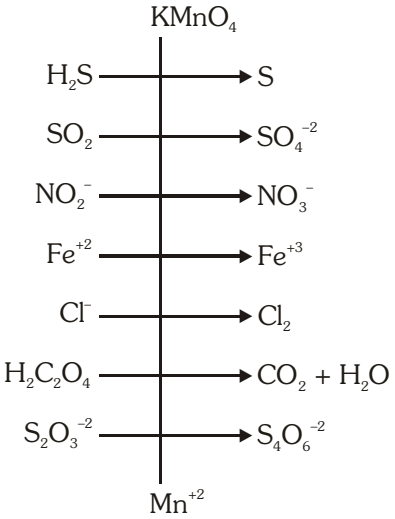
$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

- With conc. H_2SO_4 :

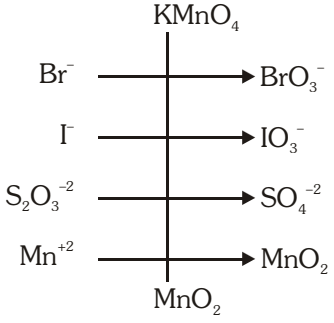
$$KMnO_4 \xrightarrow[H_2SO_4]{\text{conc.}} Mn_2O_7 \text{(explosive)}$$

- acts as oxidising agent in Acidic/Neutral/Alkaline

(a) Acidic



(b) Neutral/Weak alkaline



IMPORTANT NOTE

CHAPTER 07

Salt Analysis

WEAK GROUP

S.N.	Observation	Inference	Confirmatory Tests
1.	Brisk effervescence in cold with evolution of colourless and odourless gas	CO_3^{2-} (Carbonate)	Pass the gas in a tests tube containing small quantity of lime water. It turns milky.
2.	A colourless gas with smell of rotten eggs.	S^{2-} (sulphide)	Moisten a piece of filter paper with lead acetates solution and place it on the mouth of the test tube it turns black.
3.	A light brown gas	NO_2^- (nitrite)	(a) Pass the evolved gas through ferrous sulphate solution, it turns brown (b) Mix the given salt or mixture with a little of Kl and add dilute H_2SO_4. Evolution of violet vapours (c) Place the piece of filter paper on the mouth of test tube moistened with solution of starch, potassium iodide and acetic acid it turns blue.

STRONG GROUP

S.N.	Observation	Inference	Confirmatory Tests
1.	A colourless or yellowish green gas with pungent and suffocating smell.	Cl^- (Chloride)	Put a glass rod dipped in NH_4OH at the mouth of test tube. White dense fumes.
2.	A brown gas with pungent and suffocating smell.	Br^- (Bromide)	Salt + MnO_2 + Conc. H_2SO_4 and Heat strongly. Reddish brown vapours with pungent and suffocating smell.
3.	Violet vapours with pungent and suffocating smell.	I^- (Iodide)	A pinch of salt + MnO_2 + Conc. H_2SO_4 and Heat strongly. Violet vapours which turn starch paper blue.
4.	A brown gas with pungent and suffocating smell.	NO_3^- (Nitrate)	Salt + Conc. H_2SO_4 + Cu chips or paper pallet. Heat strongly. A reddish brown gas with pungent and suffocating smell.

DETECTION OF BASIC RADICALS (CATIONS)

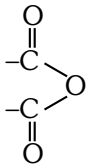
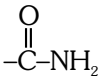
Group	Cations	Group Reagent	Precipitate formed with colour
Zero	NH_4^+	NaOH on boiling	No ppt. but ammonia gas is formed
I	Pb^{2+}	O.S + dilute HCl	$PbCl_2$ – White
II	Cu^{2+}	H_2S gas in presence of dil. HCl	CuS – Black
III	Fe^{3+} Al^{3+}	NH_4OH in presence of NH_4Cl(s)	$Fe(OH)_3$ – Reddish brown $Al(OH)_3$ – White gelatinous
IV	Ni^{2+} Zn^{2+}	H_2S in presence of NH_4OH	NiS – Black ZnS – Dirty white or slate like
V	Ba^{2+} Ca^{2+}	$(NH_4)_2CO_3$ in presence of NH_4OH	$BaCO_3$ – White $CaCO_3$ – White
VI	Mg^{2+}	Na_2HPO_4 solution + NH_4OH + NH_4Cl	$Mg(NH_4)PO_4$ – White

IMPORTANT NOTE

ORGANIC CHEMISTRY

CHAPTER 01

TABLE FOR IUPAC NOMENCLATURE

Functional group	Structure	Prefix	Suffix
Carboxylic acid		Carboxy	- oic acid *Carboxylic acid
Sulphonic acid	$-SO_3H$	Sulpho	sulphonic acid
Anhydride		×	oic-anhydride
Ester		Alkoxy carbonyl or Carbalkoxy	alkyl....oate *Carboxylate
Acid halide		Haloformyl or Halocarbonyl	- oyl halide *Carbonyl halide
Acid amide		Carbamoyl/Amido	- amide *Carboxamide
Carbonitrile/Cyanide	$-C \equiv N$	Cyano	nitrile *Carbonitrile
Isocyanide	–NC	isocyano/carbyl amino	isonitrile
Aldehyde		Formyl or Oxo	- al *Carbaldehyde
Ketone		Keto or oxo	- one
Alcohol	–OH	Hydroxy	- ol
Thio alcohol	–SH	Mercapto	thiol
Amine	$-NH_2$	Amino	amine

***Special suffix**

IMPORTANT NOTE

CHAPTER 02

ISOMERISM

DEFINITION

Compounds having same molecular formula but differ in atleast one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism : (A) Structural isomerism (B) Stereo isomerism

(A) STRUCTURAL ISOMERISM

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

TYPES OF STRUCTURAL ISOMERISM

CHAIN ISOMERISM

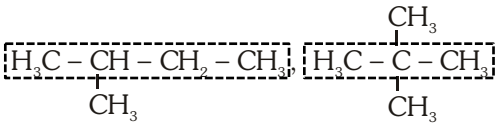
This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

Key points :

Parent carbon chain or side chain should be different.

e.g. C_5H_{12} : $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

n-pentane



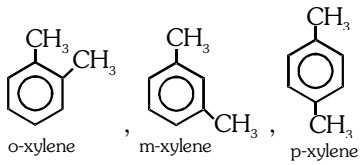
iso-pentane neo-pentane

POSITIONAL ISOMERISM

It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

Key point : Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.

e.g. $C_6H_4(CH_3)_2$:



o-xylene , m-xylene , p-xylene

FUNCTIONAL ISOMERISM

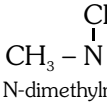
It occurs when compounds have the same molecular formula but different functional groups.

e.g. C_3H_9N : $CH_3 - CH_2 - CH_2 - NH_2$,

1-propanamine

$CH_3 - CH_2 - NH - CH_3$,

N – methylethanamine



N, N-dimethylmethanamine

METAMERISM

This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g. $C_4H_{10}O$:

$CH_3 - O - CH_2 - CH_2 - CH_3$

n-propyl methylether

$CH_3 - CH_2 - O - CH_2 - CH_3$

diethyl ether

TAUTOMERISM

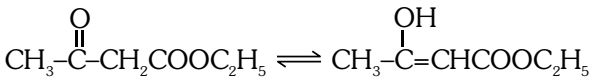
This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions :

(i) Presence of $-\overset{O}{\overset{\|}{C}}-$ or $-\overset{O}{\overset{\|}{N}} \rightarrow O$

(ii) Presence of at least one α-H atom which is attached to a saturated C-atom.

e.g. Acetoacetic ester.



keto form enol form

ENOL CONTENT ENHANCE BY:

* Acidity of α-H of keto form
* Intra molecular H-Bonding in enol form
* Resonance in enol form
* Aromatisation in enol form

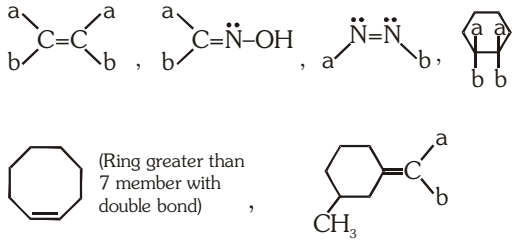
(B) STEREOISOMERISM

Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

TYPES OF STEREOISOMERISM

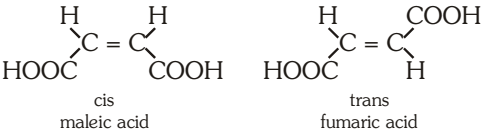
GEOMETRICAL ISOMERISM

It is due to restricted rotation and is observed in following systems



- **Cis-trans isomerism :** The *cis* compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



- General physical properties of geometrical isomer of but-2-ene

(i) Stability	*trans > cis*
(ii) Dipole moment	*cis > trans*
(iii) Boiling point	*cis > trans*
(iv) Melting point	*trans > cis*

Calculation of number of geometrical isomers :

Unsymmetrical	2^n
Symmetrical	$2^{n-1} + 2^{m-1}$ $m = \frac{n}{2}$ (If n is even) $m = \frac{n+1}{2}$ (If n is odd)

* Where n = number of sites where GI is possible.

OPTICAL ISOMERISM

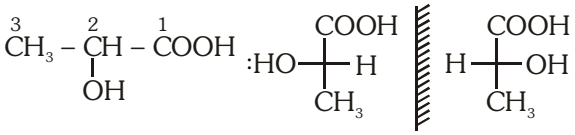
Compounds having same molecular and structural formula but different behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.

- **Types of optical isomers**
  (1) Optically active
  • dextrorotatory (d)
  • laevorotatory (ℓ)
  (2) Optically inactive
  • meso

- **Condition :**
  Molecule should be asymmetric or chiral i.e. symmetry element (POS & COS) should be absent.

- The carbon atom linked to four different groups is called **chiral carbon**.

- **Fischer projection :** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.
  Fischer projection representation of lactic acid (2-hydroxypropanoic acid)

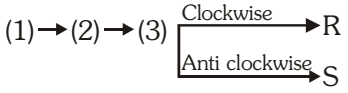


- **Configuration of optical isomer :**
  (a) Absolute configuration (R/S system)
  (b) Relative configuration (D/L system)

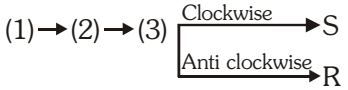
- **Determination of R/S configuration :**

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority (4) is bonded to vertical line then moving



Rule-3 If lowest priority (4) is bonded to horizontal line then moving

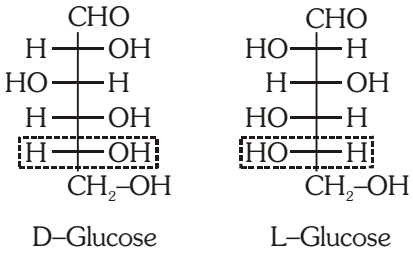


DETERMINATION OF D/L SYSTEM :

- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate, amino acid and similar compounds

Rule: Arrange parent carbon chain on the vertical line

- Placed most oxidised carbon on the top or nearest to top.
- On highest IUPAC numbered chiral carbon
  If OH group on RHS → D
  If OH group on LHS → L



D–Glucose L–Glucose

- **CIP SEQUENCE RULE :**

  The following rules are followed for deciding the precedence order of the atoms or groups :-

  (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.

  (ii) In case of isotopes, isotopes having higher atomic mass is given priority.

  (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2^{nd} atom or subsequent atoms in group.

  (iv) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.

- Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.
- **Diastereomers** are stereoisomers which are not complete mirror images of each other. They have different physical and chemical properties.
- **Meso compounds** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.
- An equimolar mixture of the enantiomers (d & ℓ) is called **racemic mixture.** The process of converting d- or ℓ- form of an optically active compound into racemic form is called **racemisation.**
- The process by which dℓ mixture is separated into d and ℓ forms with the help of chiral reagents or chiral catalyst is known as **resolution.**
- Compound containing chiral carbon may or may not be optically active but show optical isomerism.
- For optical isomer chiral carbon is not the necessery condition.

Calculation of number of optical isomers

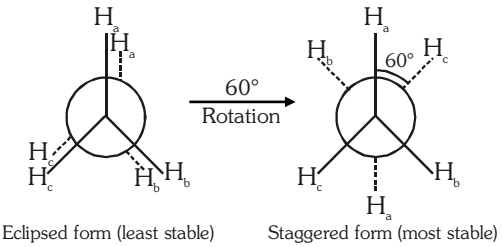
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

* Where n = no. of chiral carbon

CONFORMATIONAL ISOMERISM

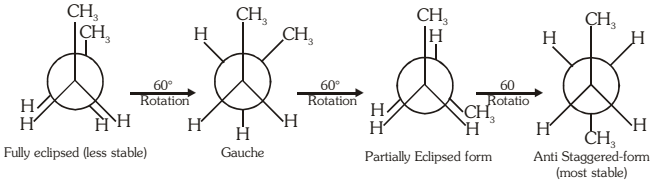
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

Confermation of ethane :



Eclipsed form (least stable) Staggered form (most stable)

- **Conformations of butane :** $\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{1}{CH_2}-\overset{1}{CH_3}$



Fully eclipsed (less stable) Gauche Partially Eclipsed form Anti Staggered-form (most stable)

- The order of stability of conformations of n-butane.

  Anti staggered>Gauche>Partially eclipsed>Fully eclipsed.

IMPORTANT NOTE

CHAPTER 03

REACTION MECHANISM

Electrophiles are electron deficient species.

eg. $H^{\oplus}$, $R^{\oplus}$, $NO_2^{\oplus}$, $X^{\oplus}$, PCl_3, PCl_5

($\overset{\oplus}{N}H_4$ and $H_3O^{\oplus}$ are not electrophile)

Nucleophiles are electron rich species.

e.g. $\overset{\ominus}{Cl}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $RO^{\ominus}$, $\overset{\ominus}{C}N$, $\ddot{N}H_3$, $R\ddot{O}H$, $CH_2=CH_2$, $CH\equiv CH$

Relative electron withdrawing order (–I order)

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH$
$> -X > -OR > -OH > -C\equiv CH > -NH_2$
$> -C_6H_5 > -CH=CH_2 > -H$

Relative electron releasing order (+I order)

$-\overset{\ominus}{N}H > -O^{\ominus} > -COO^{\ominus} > 3°alkyl > 2°alkyl > 1°alkyl > -CH_3$

RELATIVE STABILITY ORDER

(A) Stability of carbocation

- $(Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2$
- $(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$
- $CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(B) Stability of free radical

- $(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2$
- $(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(C) Stability of Carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 >$
$\overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

ACIDIC STRENGTH ∝ Stability of conjugate base

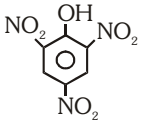
$$\propto K_a \propto \frac{1}{pK_a}$$

(i) $H_2O > CH\equiv CH > NH_3$

(ii) $CH\equiv CH > CH_2=CH_2 > CH_3-CH_3$

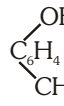
(iii) $R-SO_3H > R-COOH >$ $> R-OH$

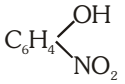
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

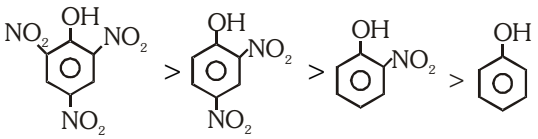
(v)  $> HCOOH > C_6H_5COOH > CH_3COOH$

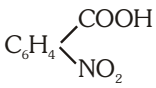
(vi) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

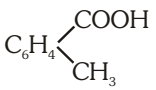
(vii) $CH_3-\underset{F}{CH}-CH_2-COOH > CH_3-\underset{F}{CH}-\underset{F}{CH}COOH > \underset{F}{CH_2}-CH_2CH_2COOH$

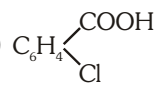
(viii)  Phenol > m > p > o

(ix)  p > o > m > Phenol

(x) 

(xi)  o > p > m > benzoic acid

(xii)  o > benzoic acid > m > p

(xiii)  o > m > p > benzoic acid

BASIC STRENGTH ∝ $K_b \propto \frac{1}{pK_b}$

- **Basic strength of amine :-**
  In aqueous medium
  $R \Rightarrow -CH_3$ $\quad 2° > 1° > 3° > NH_3$
  $R \Rightarrow -CH_2CH_3$ $\quad 2° > 3° > 1° > NH_3$
  In gaseous medium
  $R \Rightarrow -CH_3$ $\quad 3° > 2° > 1° > NH_3$
  $R \Rightarrow -CH_2CH_3$ $\quad 3° > 2° > 1° > NH_3$
- **Reactivity towards nucleophile (NAR)**
  (1) $HCHO > CH_3CHO > (CH_3)_2CO$
  (2) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$
- **Reactivity order towards acyl nucleophilic substitution reaction**
  Acid chloride > anhydride > acid > ester > amide
- **Order of electronic effect**
  Mesomeric>Hyperconjugation > Inductive effect
- **Stability of alkene ∝ no. of α-hydrogen**
  $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$
  $> \underset{\text{trans form}}{RCH=CHR} > \underset{\text{cis form}}{RCH=CHR} >$
  $RCH=CH_2 > CH_2=CH_2$
- **Heat of hydrogenation ∝** $\frac{1}{\text{Stability of alkene}}$

IMPORTANT NOTE

CHAPTER 04

PRACTICAL ORGANIC CHEMISTRY

PURIFICATION METHODS
DISTILLATION TECHNIQUES

Type :

(A) SIMPLE DISTILLATION
Conditions
(i) When liquid sample has non volatile impurities
(ii) When boiling point difference is 80 K or more.
Examples
(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)
(ii) Mixture of Ether (b.p. = 308K) & Toluene (b.p. = 384K)
(iii) Hexane (342K) and Toulene (384K)

(B) FRACTIONAL DISTILLATION
When b.p. difference is 10K
Examples
(i) Crude oil in petroleum industry
(ii) Acetone (329 K) and Methyl alcohol (338K)

(C) DISTILLATION UNDER REDUCED PRESSURE (Vacuum distillation)
When liquid boils at higher temperature and it may decompose before b.p. is attained.
Example (i) Concentration of sugar juice
(ii) Recovery of glycerol from spent lye.
(iii) Glycerol

(D) STEAM DISTILLATION
When the substance is immiscible with water and steam volatile.
Example :
(i) Aniline is separated from water
(ii) o and p-Nitrophenol

$P = P_1 + P_2$
Vapour pressure — Vapour pressure of Organic liquid — Vapour pressur of water

LASSAIGNE'S METHOD
(detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	Na + C + N $\xrightarrow{\Delta\downarrow}$ NaCN	(NaCN+$FeSO_4$+NaOH) boil and cool +$FeCl_3$+conc. HCl $\rightarrow$ $Fe_4[Fe(CN)_6]_3$ Ferri-ferrocyanide Prussian blue colour
Sulphur	2Na + S $\xrightarrow{\Delta\downarrow}$ Na_2S	(i) $Na_2S + Na_2[Fe(CN)_5NO]$ sodium nitrosopruside $\rightarrow Na_4[Fe(CN)_5NOS]$ a deep violet colour (ii) $Na_2S+CH_3COOH+(CH_3COO)_2Pb \rightarrow PbS\downarrow$ Black ppt.
Halogen	Na + X $\xrightarrow{\Delta\downarrow}$ NaX	$NaX + HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Pale yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together	Na+C+N+S $\xrightarrow{\Delta\downarrow}$ NaCNS Sodium thiocyanate (Blood red colour)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Estimation of carbon and hydrogen - Leebig's method

$$C_xH_y + \frac{x+y}{4}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of org. compd}} \times 100$$

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{wt. of } H_2O}{\text{wt. of org compd}} \times 100$$

Note : This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

ESTIMATION OF NITROGEN

Duma's method :

The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

$$\% \text{ of } N = \frac{28}{22400} \times \left(\frac{\text{Vol. of } N_2 \text{ collected at N.T.P.}}{\text{Wt. of organic compound}} \right) \times 100$$

Note : This method can be used to estimate nitrogen in all types of organic compounds

Kjeldahl's method :

In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\textbf{\% of N} = \frac{1.4 \times \text{volume (ml) of } H_2SO_4 \text{ used for Neutralisation} \times \text{normality of acid}}{\text{wt of organic compound}}$$

Note : This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (–N=N–), nitrogen in the ring (pyridine, quinole etc.) and nitrogroup $–NO_2$. Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

IMPORTANT NOTE

CHAPTER 05

DISTINCTION BETWEEN PAIRS OF COMPOUNDS

UNSATURATION TEST

(a) Double/Triple bonded Compounds (C=C)/(C≡C) + Br_2 in CCl_4 (Brown colour) → Colourless compound

- $R–CH=CH–R + Br_2 \xrightarrow{CCl_4} R–\underset{Br}{\overset{}{CH}}–\underset{Br}{\overset{}{CH}}–R$
  (Alkene) (Brown) (Colourless)

- $R–C\equiv C–R + Br_2 \xrightarrow{CCl_4} R–\underset{Br}{\overset{Br}{C}}=\underset{Br}{\overset{Br}{C}}–R$
  (Alkyne) (Brown) (Colourless)

(b) Double/Triple bonded Compounds + Bayer's reagent – 1% alkaline $KMnO_4$ (Pink colour) ⟶ Brown precipitate

- $R–CH=CH–R + KMnO_4 \longrightarrow R–\underset{OH}{\overset{}{CH}}–\underset{OH}{\overset{}{CH}}–R + MnO_2$
  (Alkene) (Cold, dilute) (Colourless) Brown ppt

- $R–C\equiv C–R' + KMnO_4 \xrightarrow[\text{(Hot, dilute)}]{} MnO_2 + RCOOH + R'COOH$
  Brown ppt.

- $R–C\equiv C–H + KMnO_4 \xrightarrow[\text{(Hot, dilute)}]{} MnO_2 + RCOOH + CO_2 + H_2O$
  (Alkyne) Brown ppt. (Colourless)

Baeyer's reagent is cold, dilute $KMnO_4$ solution having pink colour.

Note : The above test are not given by Benzene. Although it has unsaturation.

TEST FOR TERMINAL ALKYNE

Terminal alkyne

- Ammonical silver nitrate → White ppt.
- Ammonical cuprous chloride → Red ppt.

$NH_4NO_3 + H_2O + R–C\equiv\overset{\ominus}{C}\ \overset{\oplus}{Ag}$ ← $AgNO_3 + NH_4OH$
White ppt.

$R–C\equiv CH$
Terminal alkyne

$NH_4Cl + H_2O + R–C\equiv\overset{\ominus}{C}\ \overset{\oplus}{Cu}$ ← $Cu_2Cl_2 + NH_4OH$
Red ppt.

NATURE OF X-GROUP IN C–X BOND

$R–X + \text{aqueous KOH} \longrightarrow R–OH + KX \xrightarrow[AgNO_3]{HNO_3} \underset{\text{Precipitate}}{AgX}$

If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

DISTINCTION BETWEEN 1°, 2° & 3° ALCOHOLS

- $R–\underset{R}{\overset{R}{C}}–OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R–\underset{R}{\overset{R}{C}}–Cl$
  Tertiary alcohol — Cloudiness (Turbidity) appears immediately

- $R–\underset{}{\overset{R}{CH}}–OH \xrightarrow[\text{Room temperature}]{\text{Lucas reagent}} R–\underset{}{\overset{R}{CH}}–Cl$
  Secondary alcohol — Cloudiness appears within five minutes

- $R–CH_2–OH \xrightarrow[\text{Heat}]{\text{Lucas reagent}} R–CH_2–Cl$
  Primary alcohol — Cloudiness appears after 30 minute or no reaction at room temperature

Lucas reagent is anhydrous $ZnCl_2$ + conc. HCl.

HALOFORM REACTION IN ALCOHOL

- $H_3C–\underset{}{\overset{OH}{CH}}–R$ type of alcohols give iodoform test.

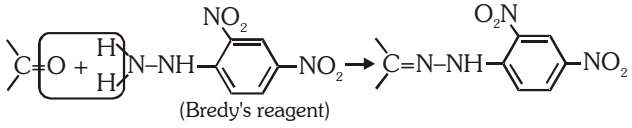
- $H_3C–\underset{}{\overset{OH}{CH}}–R + I_2 \xrightarrow[\text{Iodoform test}]{NaOH} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + RCOONa$

PHENOL

Phenol + ferric chloride ⟶ Violet colouration
neutral

CARBONYL GROUP

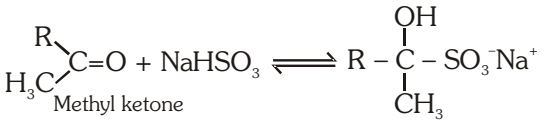
- Carbonyl compound + 2,4-DNP (Brady's reagent) ⟶ Yellow/orange crystal



(Bredy's reagent)

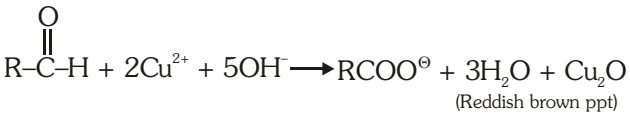
- All aldehydes and only aliphatic methyl ketones + $NaHSO_3$ → White crystalline bisulphite (Water soluble).

$\underset{\text{Aldehyde}}{\overset{R}{\underset{H}{}}C=O} + NaHSO_3 \rightleftharpoons R–\underset{H}{\overset{OH}{C}}–SO_3^-Na^+$

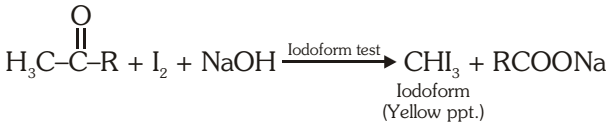


- Aldehyde + Tollen's reagent ⟶ Silver mirror

- Aldehyde + Fehling's solution → Reddish brown precipitate

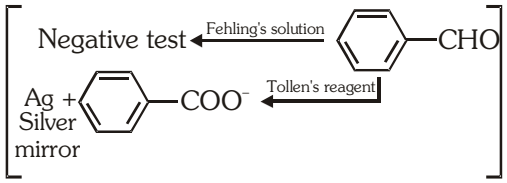


- $H_3C-\overset{O}{\overset{\|}{C}}-$ group also give iodoform test

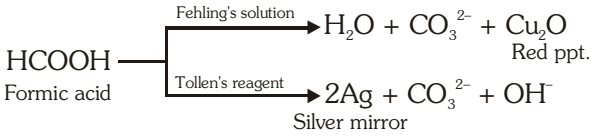


AROMATIC ALDEHYDE GROUP

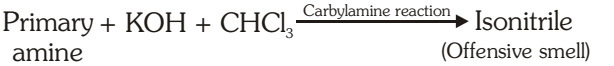
- Aromatic aldehyde + Tollen's reagent → Silver mirror
- Aromatic aldehyde + Fehling's sol^n → Negative test



FORMIC ACID



AMINES (1°)

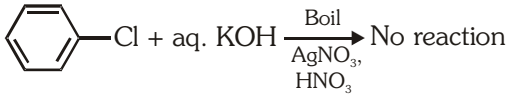


Amines (1°, 2° & 3°) (Hinsberg's test)

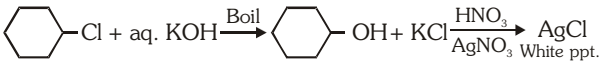
- Primary amine + Benzenesulphonyl chloride ⟶ Precipitate $\xrightarrow{KOH}$ soluble
- Secondary amine + Benzenesulphonyl chloride ⟶ Precipitate $\xrightarrow{KOH}$ insoluble
- Tertiary amine + Benzenesulphonyl chloride → No reaction

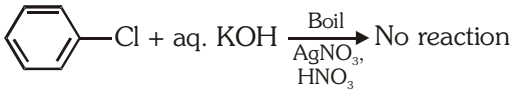
Note : Benzenesulphonyl chloride is called Hinsberg's reagent.

Chloroethane and chlorobenzene

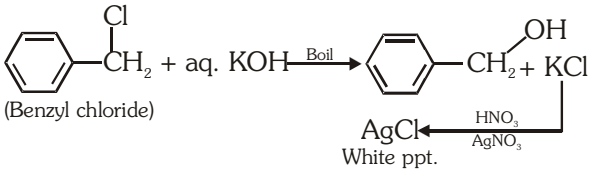
- $C_2H_5-Cl + aq.\ KOH \xrightarrow{Boil} C_2H_5-OH + KCl \xrightarrow[AgNO_3]{HNO_3} \underset{\text{White ppt.}}{AgCl}$
- 

Chlorocyclohexane and chlorobenzene

- 

- 

Benzyl chloride and chlorobenzene

- 

-

n-Propyl alcohol and iso-propyl alcohol

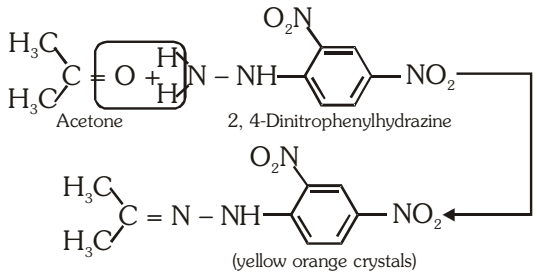
- $CH_3CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2Cl$
  No cloudiness at room temp.
- $H_3C-\underset{OH}{CH}-CH_3 \xrightarrow[HCl]{ZnCl_2} H_3C-\underset{Cl}{CH}-CH_3$
  Cloudiness within 5 minutes

Ethyl alcohol and methyl alcohol (Iodoform test)

- $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa$
- $CH_3OH + 4I_2 + 6NaOH \rightarrow$ No yellow ppt.

Ethyl alcohol and acetone

(By 2, 4 – DNP)

- 

- $C_2H_5OH \xrightarrow{2,4\text{–DNP}}$ No reaction

Phenol and ethyl alcohol (Neutral $FeCl_3$)

- Phenol + Neutral ferric chloride → Violet colouration
- CH_3CH_2OH + Neutral ferric chloride → No violet color

Benzoic acid and phenol ($NaHCO_3$)

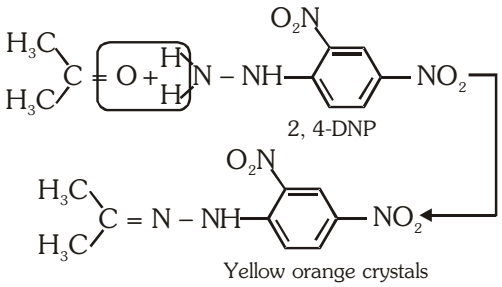
- Benzoic acid + Sodium bicarbonate → effervescence

$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$

- Phenol + Sodium bicarbonate → No effervescence

(Phenol is less acidic than benzoic acid)

Propanone and propanol (2, 4 - DNP)

- 

- Propanol + 2,4-Dinitrophenylhydrazine → No crystals

Ethanal and propanal (Iodoform test)

- $H_3C-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}} \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + HCOONa$

Ethanal

- $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Propanal

Propanal and propanone (Tollen's and Fehling reagent)

- Propanal + Tollen's reagent ⟶ Silver mirror

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow CH_3CH_2COO^- + 2H_2O + 4NH_3 + 2Ag\downarrow$$

(Silver mirror)

- Propanal + Fehling's solution → Reddish brown precipitate

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

(Reddish brown ppt.)

- Propanone → Fehling's solution → Negative
  Propanone → Tollen's reagent → Negative

Pentan-2-one and pentan-3-one (Iodoform test)

- $H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$

(Pentan-2-one)

$\underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + CH_3CH_2CH_2COONa$

- $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.

Pentan-3-one

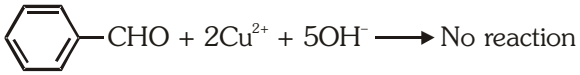
Propanal and benzaldehyde (Fehling solution)

- Propanal + Fehling's solution → Reddish brown ppt

$$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CH_2COO^- + 3H_2O + Cu_2O$$

Fehling's solution

- Benzaldehyde + Fehling's solution → No precipitate



Methanoic acid and ethanoic acid (Tollen's & Fehling solution)

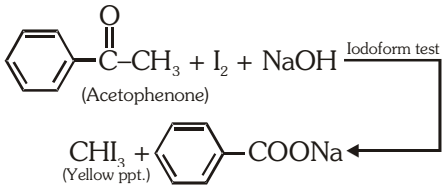
- HCOOH (Methanoic acid) → Fehling's solution → $H_2O + CO_3^{2-} + Cu_2O$
  HCOOH (Methanoic acid) → Tollen's reagent → $2Ag\downarrow + CO_3^{2-} + H_2O$

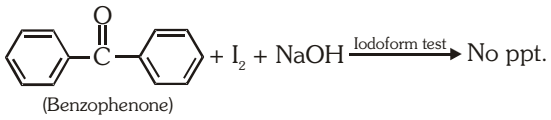
- Ethanoic acid → Fehling's solution → No reddish brown ppt.
  Ethanoic acid → Tollen's reagent → No silver mirror

Ethanal and methanal (Iodoform test)

- $CH_3CHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}} CHI_3 + HCOONa$
  Ethanal → Iodoform (Yellow ppt.)
- $HCHO + I_2 + NaOH \xrightarrow{\text{Iodoform test}}$ No yellow ppt.
  Methanal

Acetophenone and benzophenone (Iodoform test)

- 

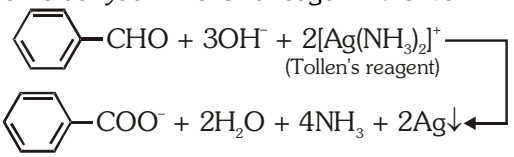
- 

Benzoic acid and ethylbenzoate

- $C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2\uparrow + H_2O$
  effervescence
- Ethyl benzoate + Sodium bicarbonate → No effervescence

Benzaldehyde and acetophenone (Tollen's test)

- Benzaldehyde + Tollen's reagent → Silver mirror

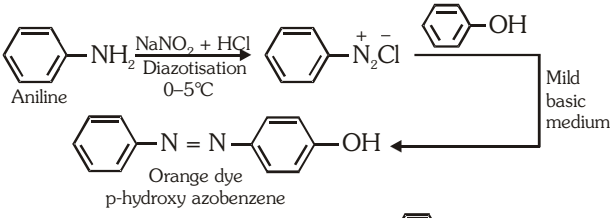


- Acetophenone + Tollen's reagent → No silver mirror

Methyl amine and dimethyl amine (Isocyanide test)

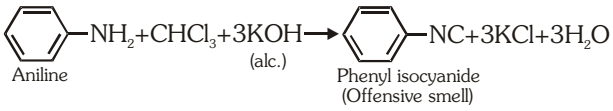
- $CH_3NH_2 + CHCl_3 + 3KOH \rightarrow CH_3NC + 3KCl + 3H_2O$
  Methyl amine (alc.) Methyl isocyanide (Offensive smell)
- $H_3C{-}\underset{\text{Di-methyl amine}}{\overset{\overset{CH_3}{|}}{NH}} + CHCl_3 + 3KOH(alc.) \rightarrow$ No offensive smell

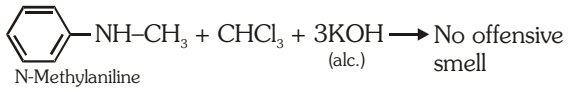
Aniline and ethyl amine (Diazotisation)

- 

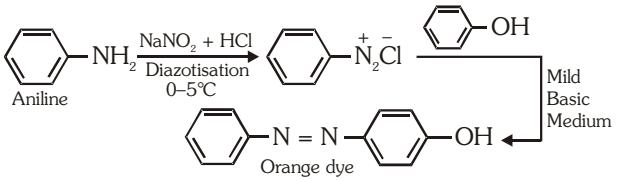
- $CH_3CH_2NH_2 \xrightarrow{NaNO_2 + HCl} CH_3CH_2OH$ (OH)
  Ethyl amine → No Orange dye

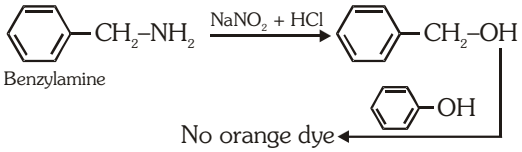
Aniline and N-methylaniline (Isocyanide test)

- 

- 

Aniline & Benzylamine (Diazotisation + phenol)

- 

- 

Glucose and fructose

- $Glucose + \underset{(brown)}{Br_2} + H_2O \rightarrow \underset{(colorless)}{Gluconic\ acid} + 2HBr$
- $Fructose + \underset{(brown)}{Br_2} + H_2O \rightarrow$ No change in colour

Glucose and sucrose

- Glucose + Tollen's reagent ⟶ Silver mirror
- Sucrose + Tollen's reagent ⟶ No silver mirror

Glucose and starch

- Glucose + Fehling's solution ⟶ Red ppt.
- Starch + Fehling's solution ⟶ No red ppt.

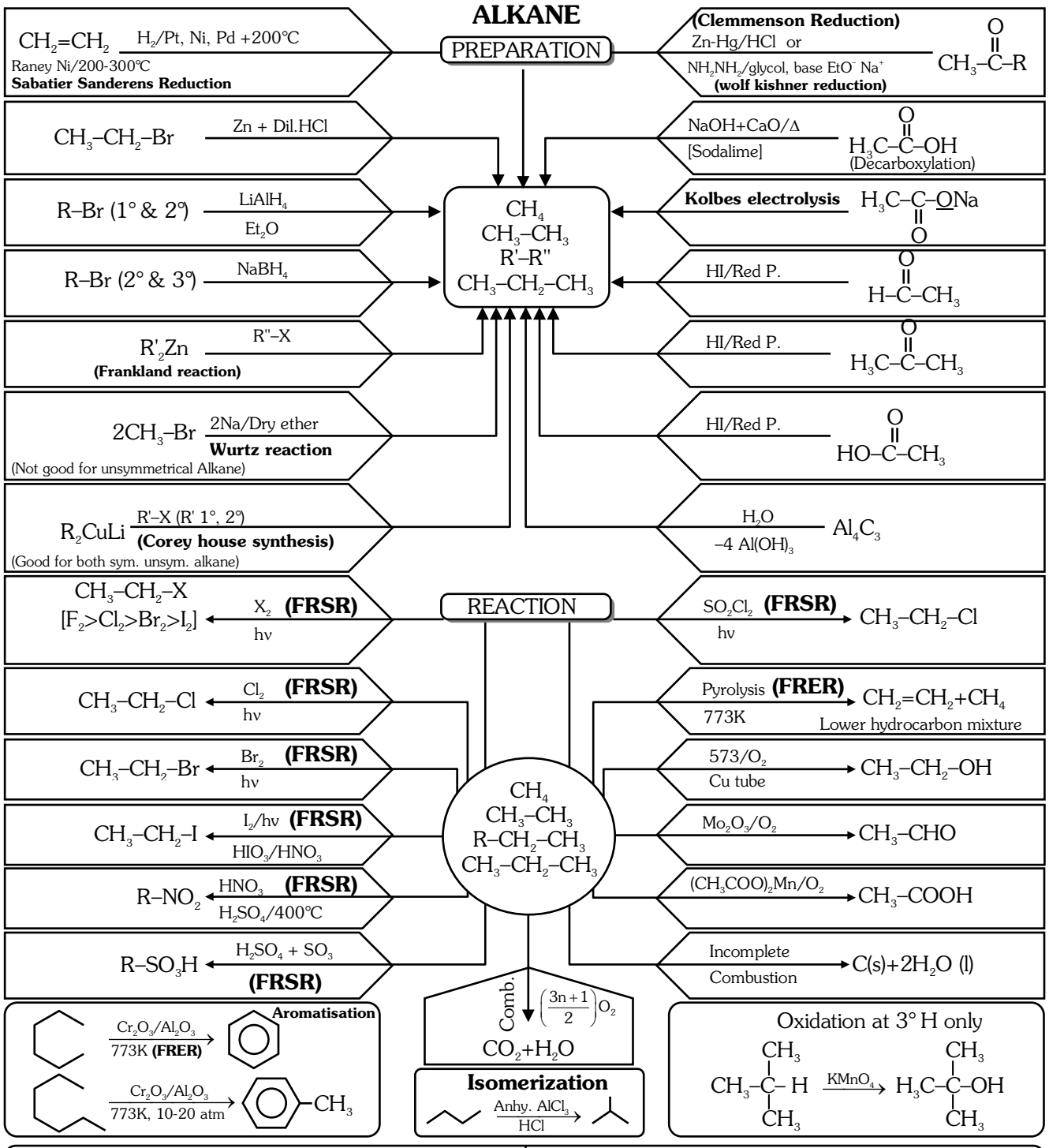
OR

- Glucose + I_2 solution ⟶ No blue colour
- Starch + I_2 solution ⟶ Blue colour

IMPORTANT NOTE

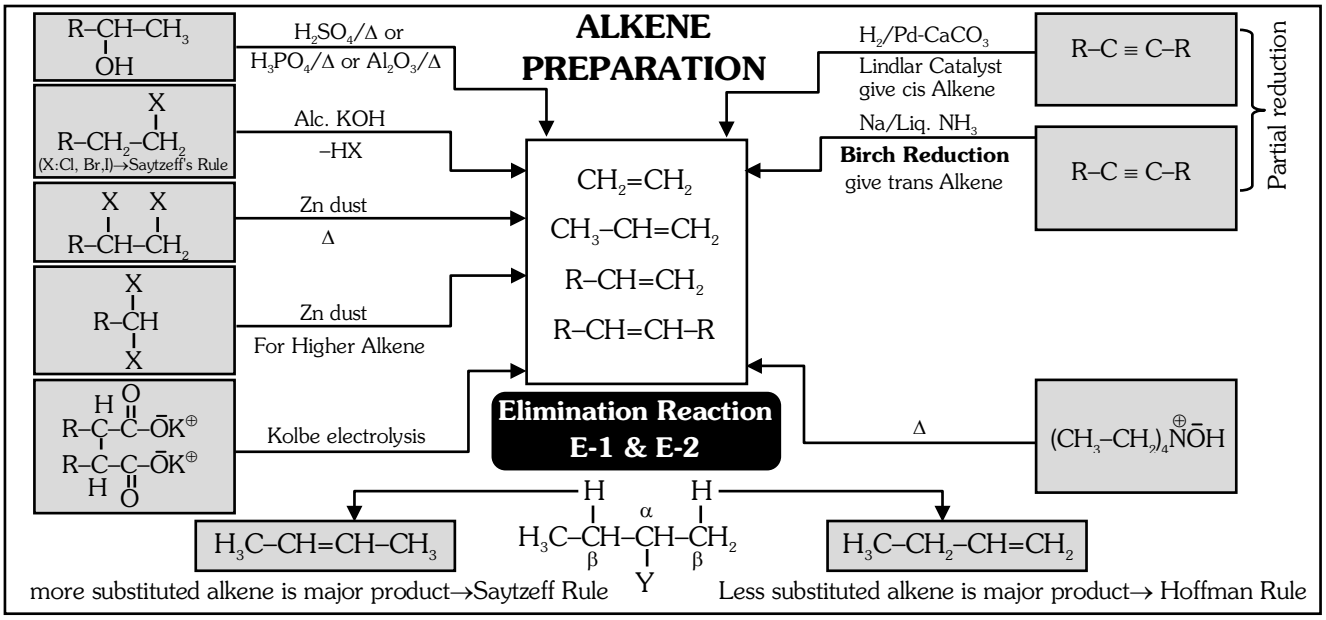
CHAPTER 06

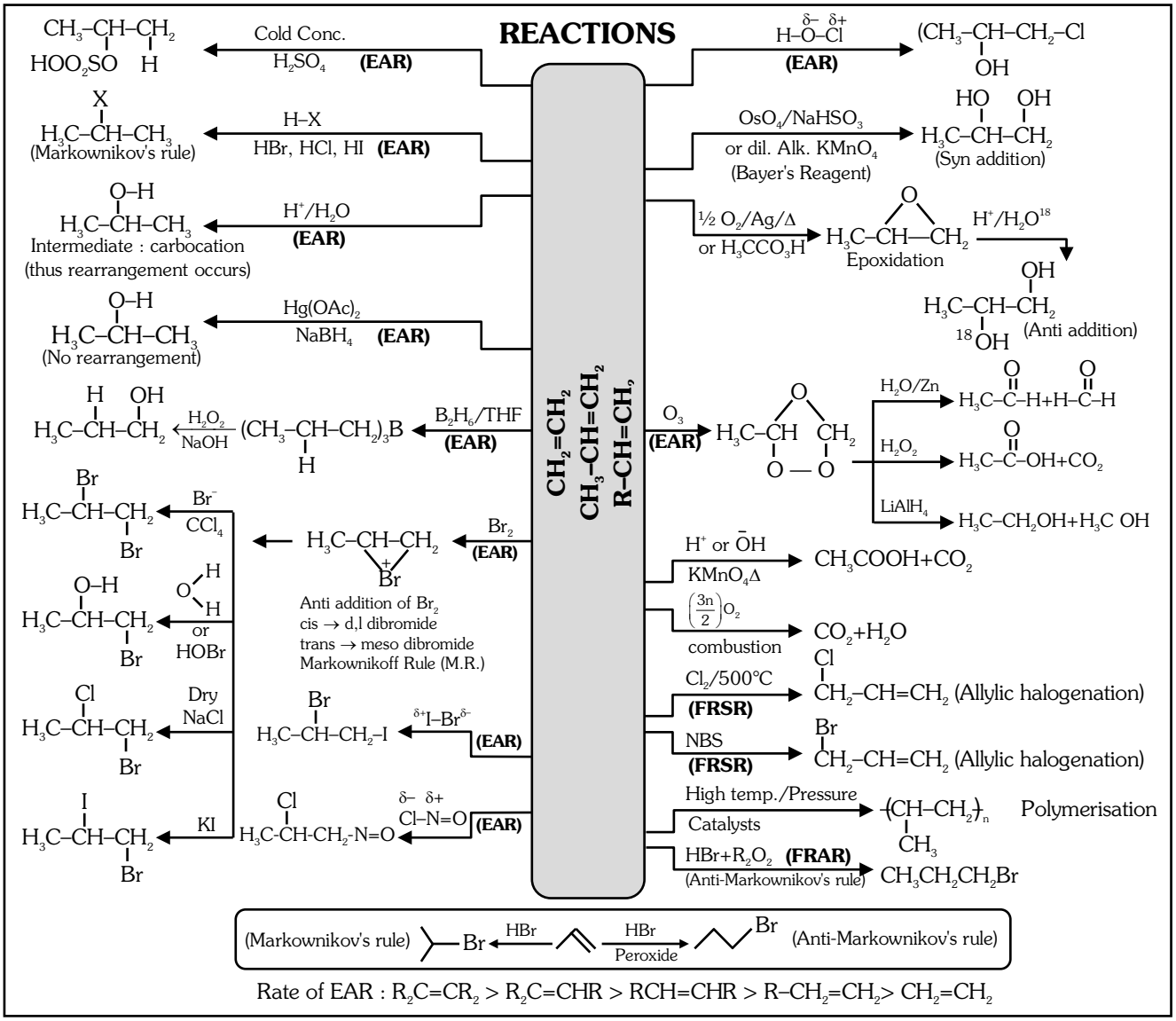
HYDROCARBON



- Reactivity of alkane towards free radical halogenation is ∝ stability of free radical $C_6H_5-CH_3>CH_2=CH-CH_3>(CH_3)_3CH > CH_3-CH_2-CH_3>CH_3-CH_3>CH_4$
- Reactivity of halogen towards free radical substitution
  $F_2 > Cl_2 > Br_2 > I_2$
- Knocking tendency of petroleum as fuel decrease with increase in side chain. Straight chain > Branched chain
  Knocking tendency is in the order
  Olefin > cycloalkane > aromatic

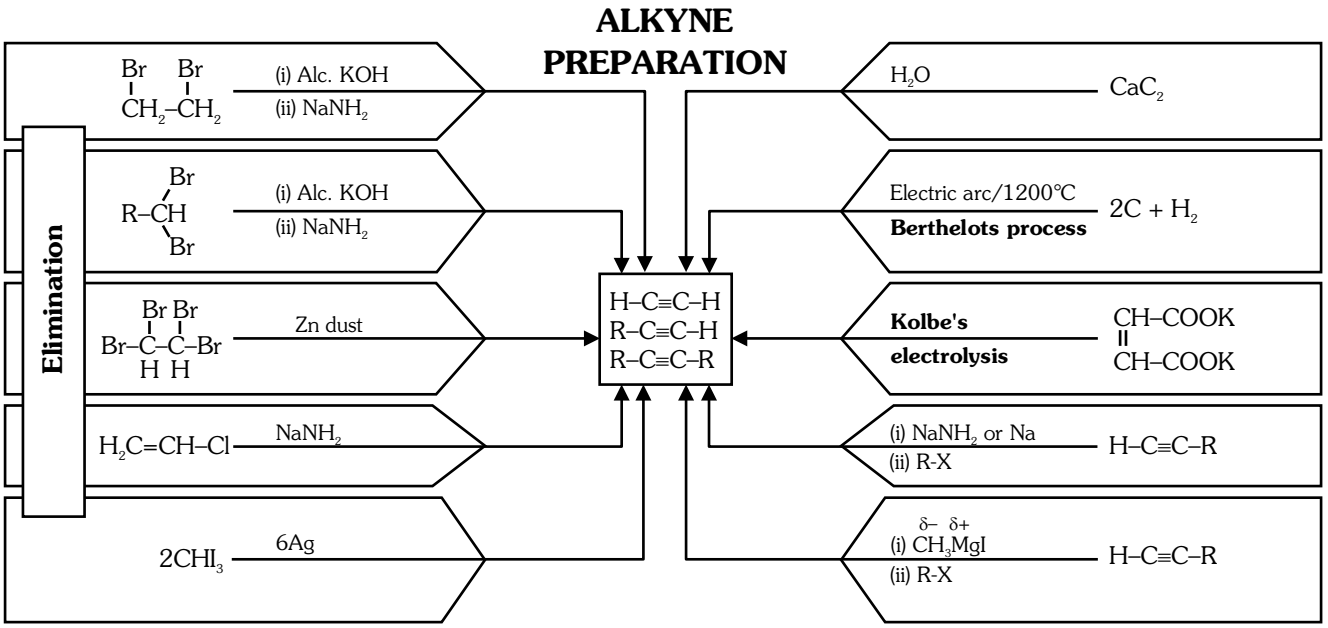
- Boiling point decrease with increase in number of side chain.
  $CH_3-CH_2-CH_2-CH_2-CH_3 >$ normal
  $> CH_3-CH(CH_3)-CH_2-CH_3 >$ iso
  $> CH_3-C(CH_3)(CH_3)-CH_3$ neo

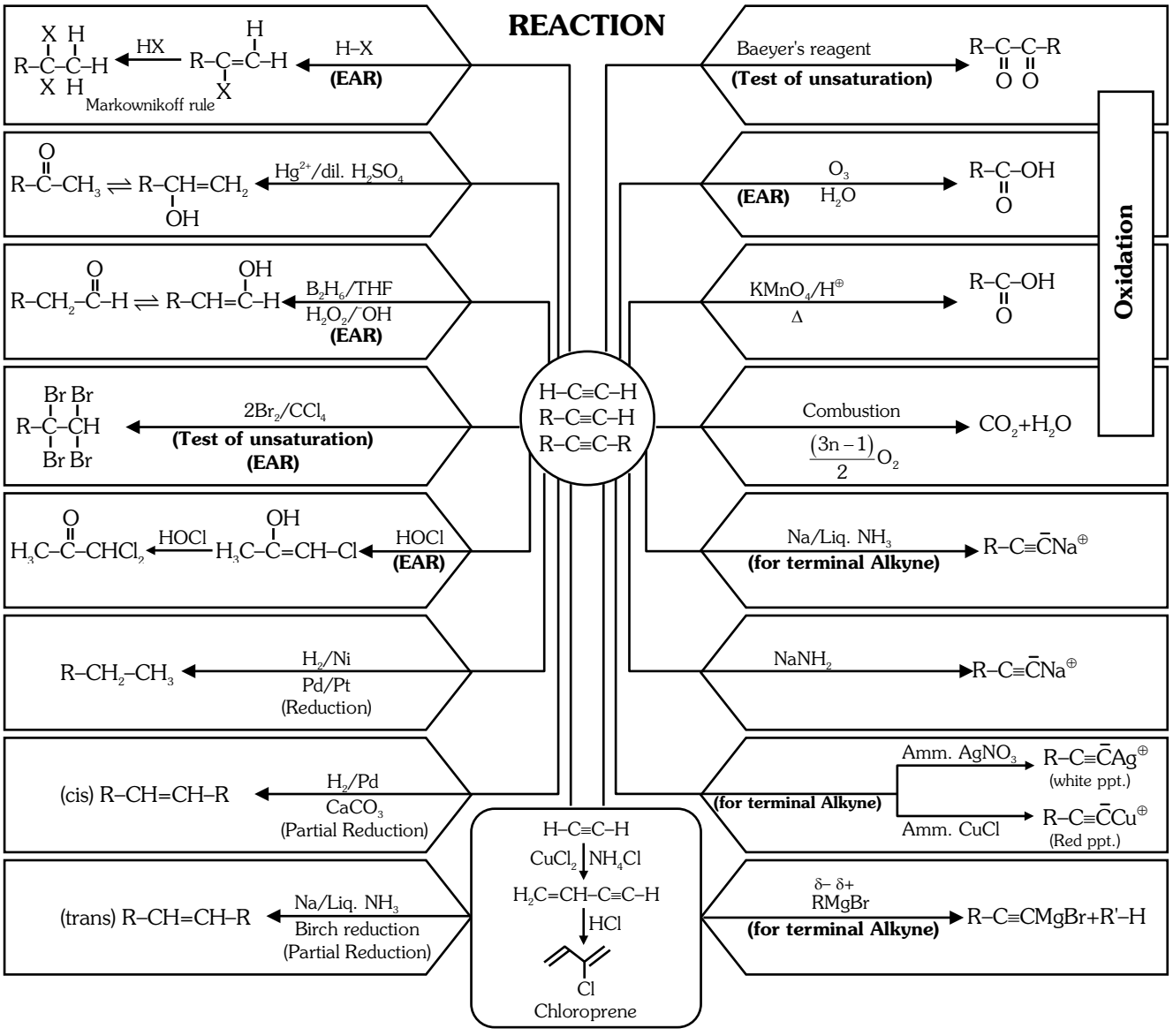




Rate of EAR : $R_2C=CR_2 > R_2C=CHR > RCH=CHR > R-CH_2=CH_2 > CH_2=CH_2$

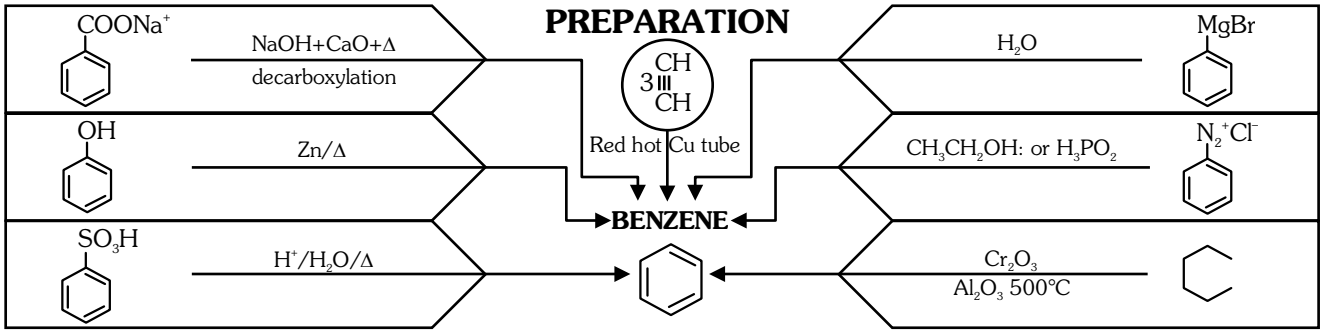
- Order of reactivity of olefins for hydrogenation $CH_2=CH_2 > R-CH=CH_2$ (Reverse of stability)
- Order of reactivity of alkene towards hydration $CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH_2 > CH_3-CH=CH_2 > CH_2=CH_2$


ALKYNE PREPARATION
Elimination
Br Br
CH2–CH2
(i) Alc. KOH
(ii) NaNH2
H2O
CaC2
R–CH
Br
Electric arc/1200°C
Berthelots process
2C + H2
Br Br
Br–C–C–Br
H H
Zn dust
H–C≡C–H
R–C≡C–H
R–C≡C–R
Kolbe's electrolysis
CH–COOK
CH–COOK
H2C=CH–Cl
NaNH2
(i) NaNH2 or Na
(ii) R-X
H–C≡C–R
2CHI3
6Ag
δ– δ+
(i) CH3MgI
(ii) R-X
H–C≡C–R


REACTION
X H
R–C–C–H
X H
HX
Markownikoff rule
R–C=C–H
X
H–X
(EAR)
Baeyer's reagent
(Test of unsaturation)
R–C–C–R
O O
Oxidation
R–C–CH3 ⇌ R–CH=CH2
OH
Hg2+/dil. H2SO4
O3
H2O
(EAR)
R–C–OH
R–CH2–C–H ⇌ R–CH=C–H
B2H6/THF
H2O2/ OH
(EAR)
KMnO4/H⊕
Δ
Br Br
R–C–CH
Br Br
2Br2/CCl4
(Test of unsaturation)
(EAR)
H–C≡C–H
R–C≡C–H
R–C≡C–R
Combustion
(3n – 1)/2 O2
CO2+H2O
H3C–C–CHCl2
HOCl
H3C–C=CH–Cl
HOCl
(EAR)
Na/Liq. NH3
(for terminal Alkyne)
R–C≡C⁻Na⊕
R–CH2–CH3
H2/Ni
Pd/Pt
(Reduction)
NaNH2
R–C≡C⁻Na⊕
(cis) R–CH=CH–R
H2/Pd
CaCO3
(Partial Reduction)
Amm. AgNO3
R–C≡C⁻Ag⊕
(white ppt.)
(for terminal Alkyne)
Amm. CuCl
R–C≡C⁻Cu⊕
(Red ppt.)
H–C≡C–H
CuCl2 NH4Cl
H2C=CH–C≡C–H
HCl
Cl
Chloroprene
(trans) R–CH=CH–R
Na/Liq. NH3
Birch reduction
(Partial Reduction)
δ– δ+
RMgBr
(for terminal Alkyne)
R–C≡CMgBr+R'–H

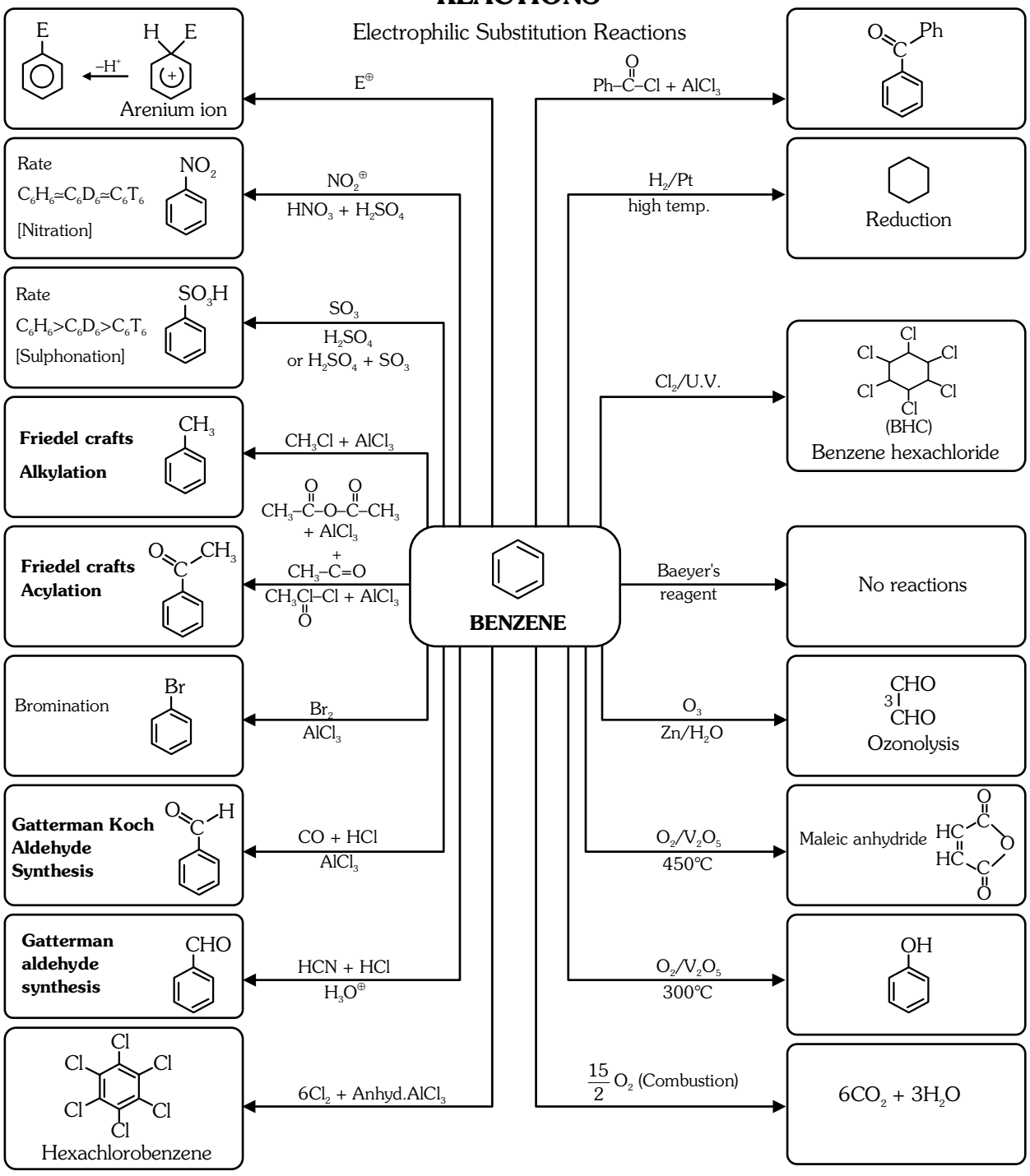
BENZENE

PREPARATION



REACTIONS

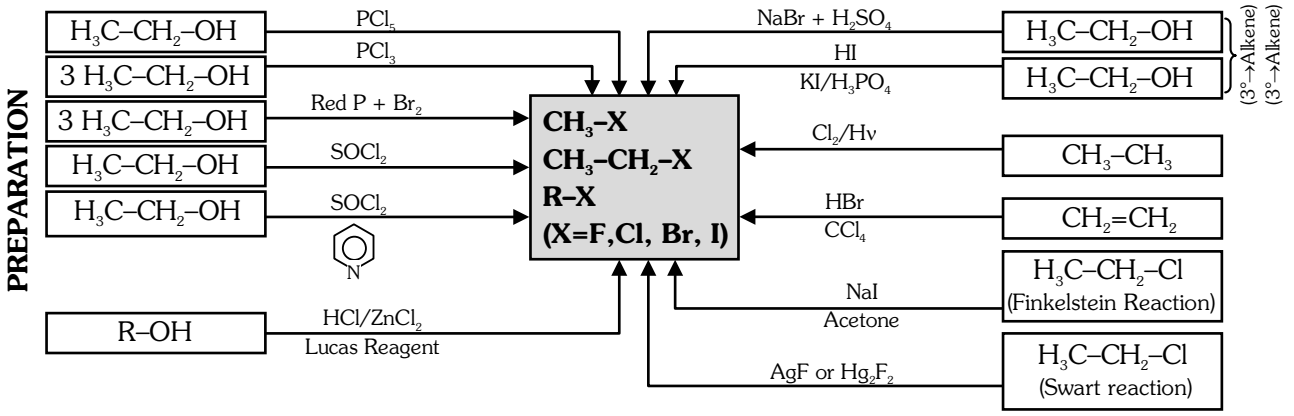
Electrophilic Substitution Reactions

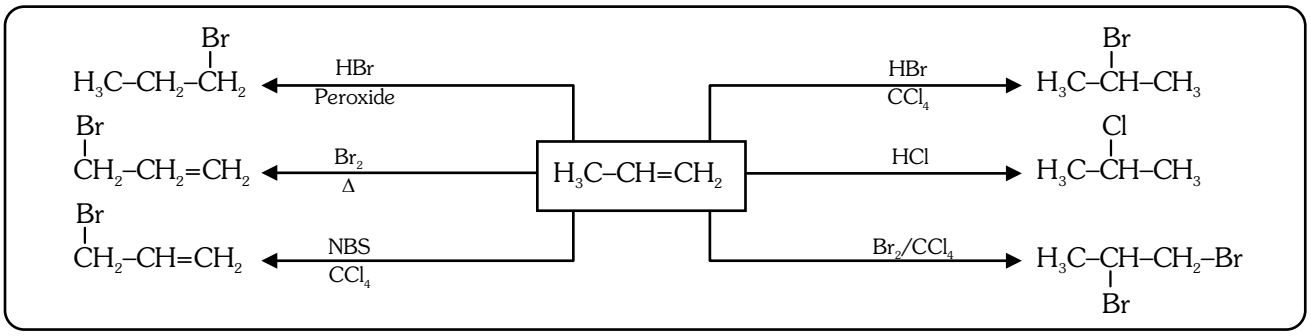


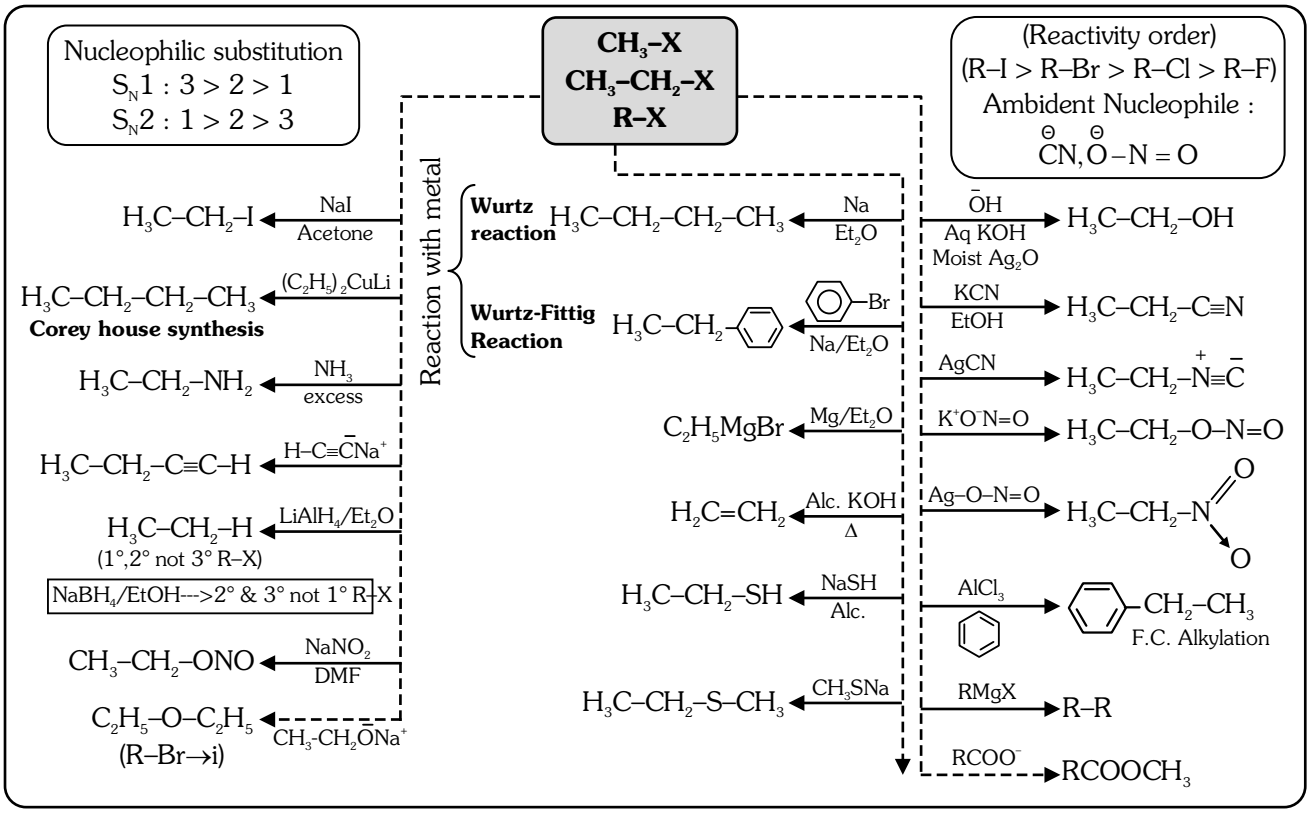
IMPORTANT NOTE

CHAPTER 07

HALOALKANE





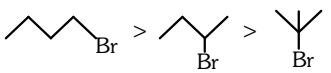


PHYSICAL PROPERTIES

(1) Dipole moment : $CH_3–Cl > CH_3–F > CH_3–Br > CH_3–I$

(2) Bond enthalpies : $CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I$

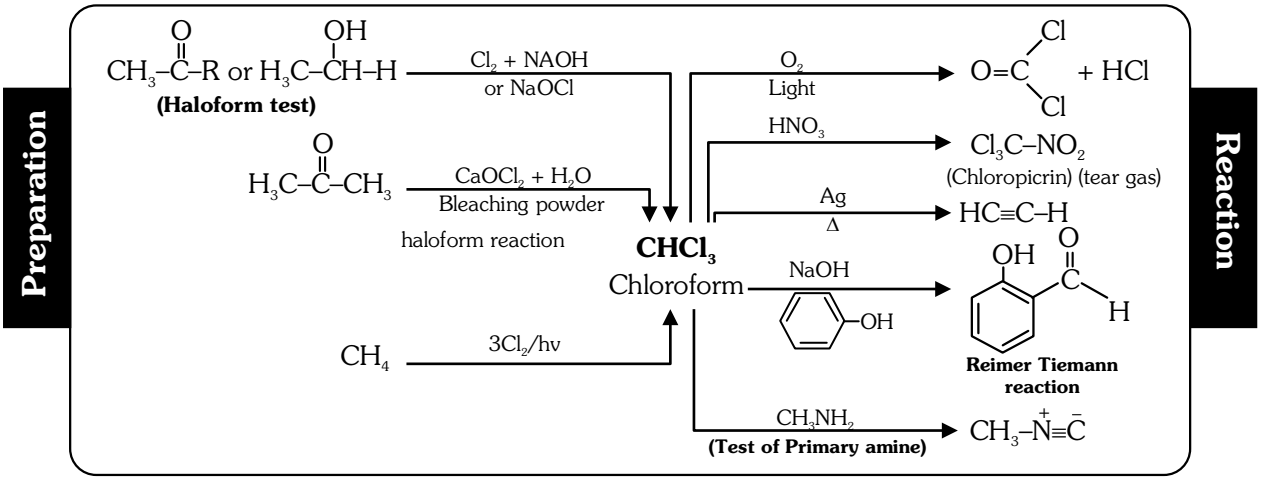
(3) Boiling point : R–I > R–Br > R–Cl > R–F



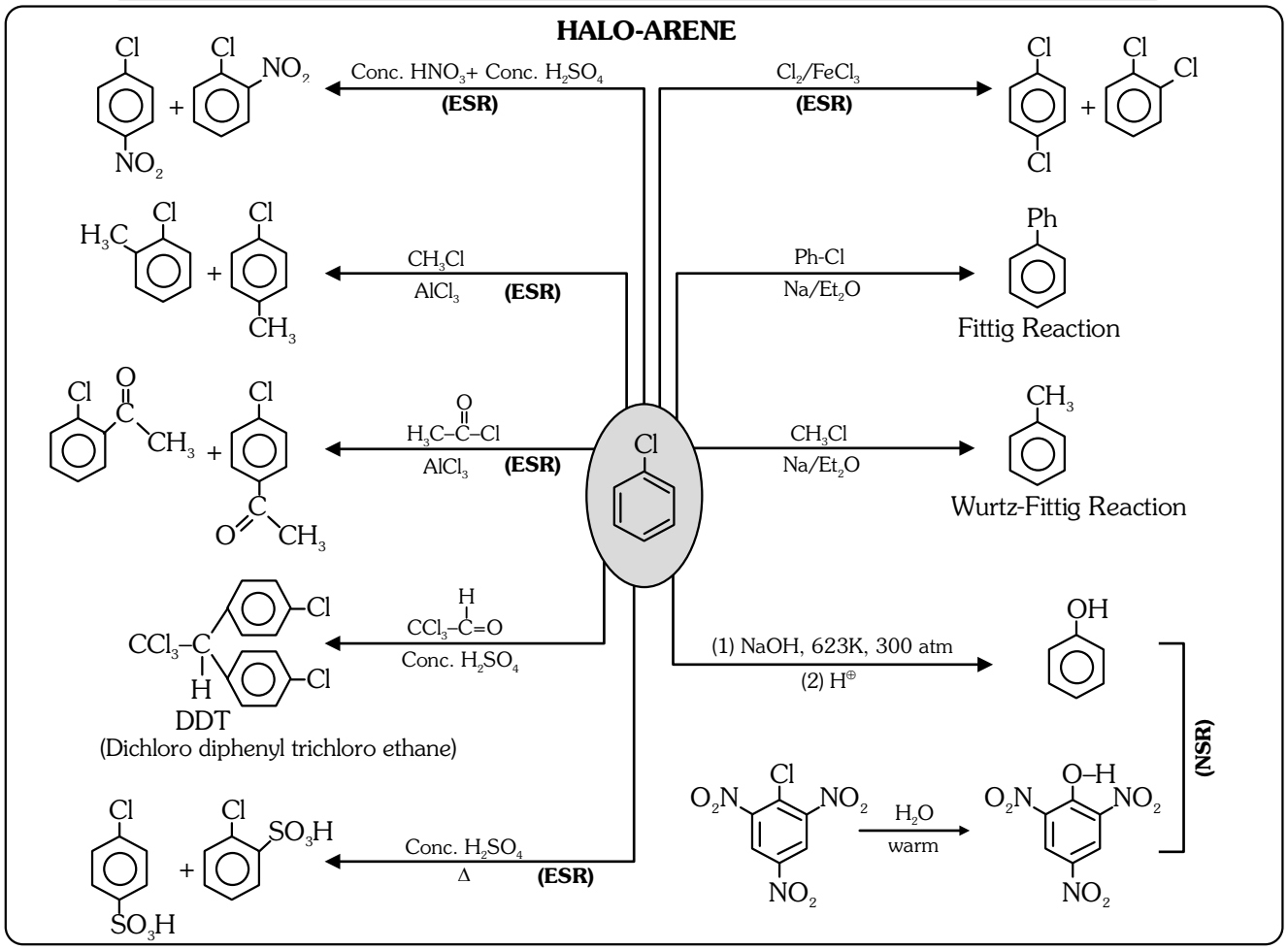
(4) Density :

$n–C_3H_7Cl < n–C_3H_7Br < n–C_3H_7I$

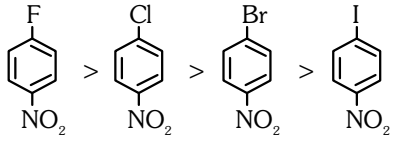
TRI-HALOALKANE

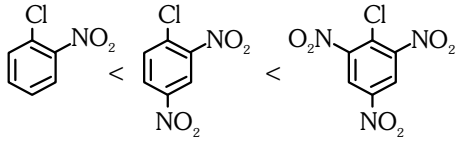


HALO-ARENE

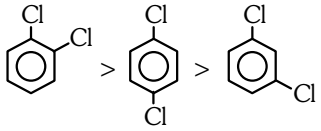


(A) [Reactivity toward Nucleophile]

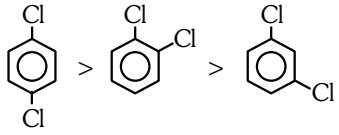
(i) 

(ii) 

(B) Boiling point



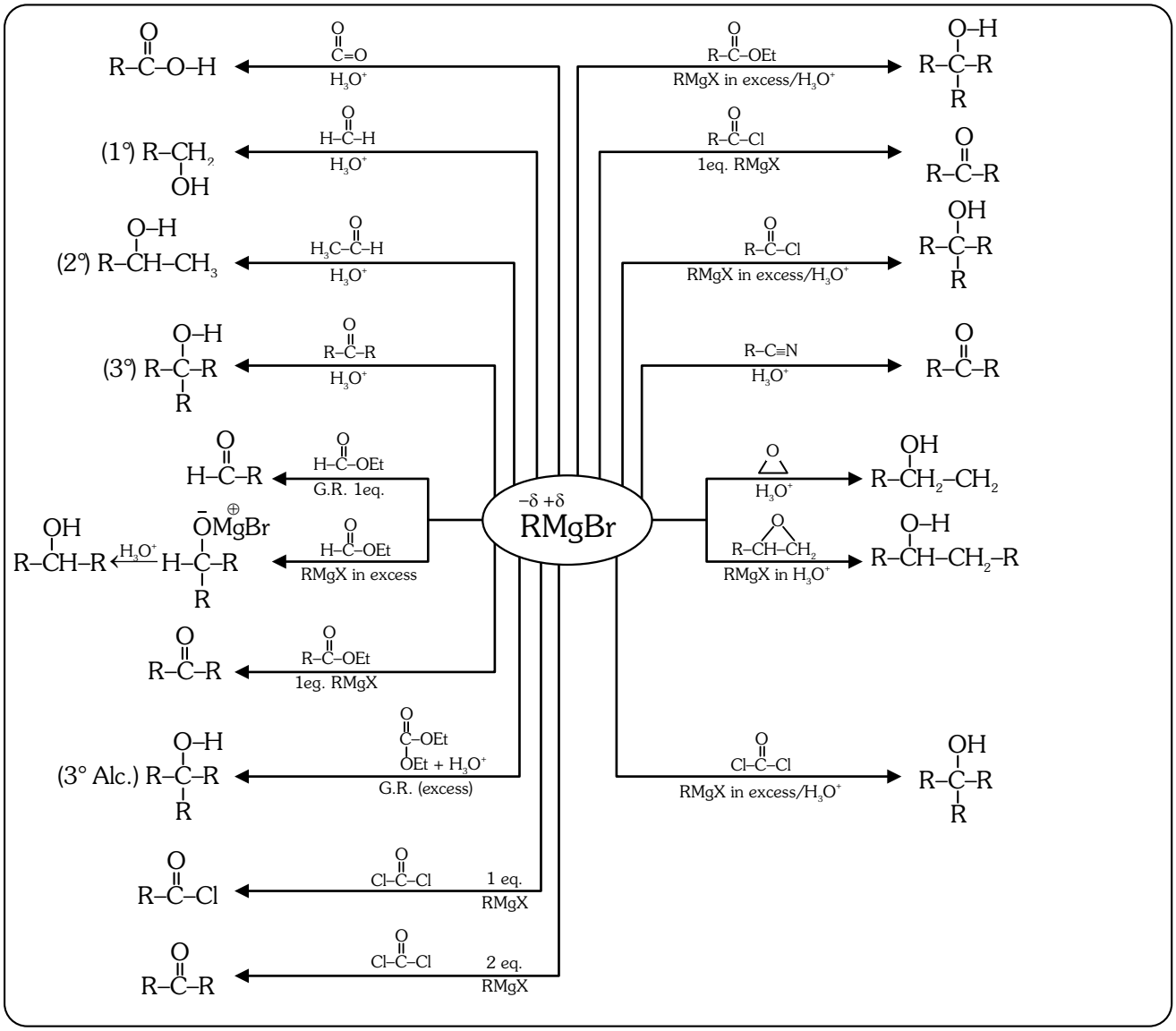
(C) Melting point



GRIGNARD REAGENT

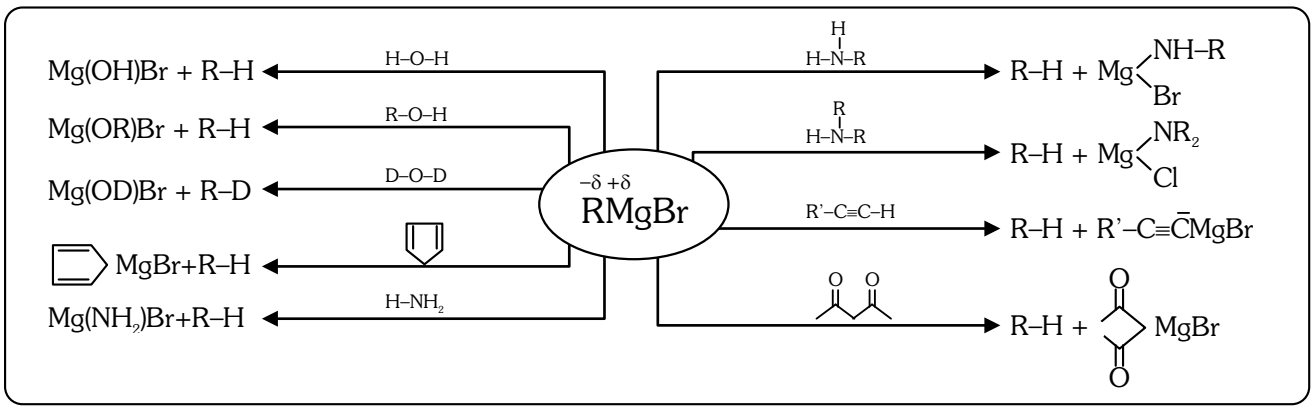
REACTION

GRIGNARD REAGENT as Nucleophile



GRIGNARD REAGENT as BASE

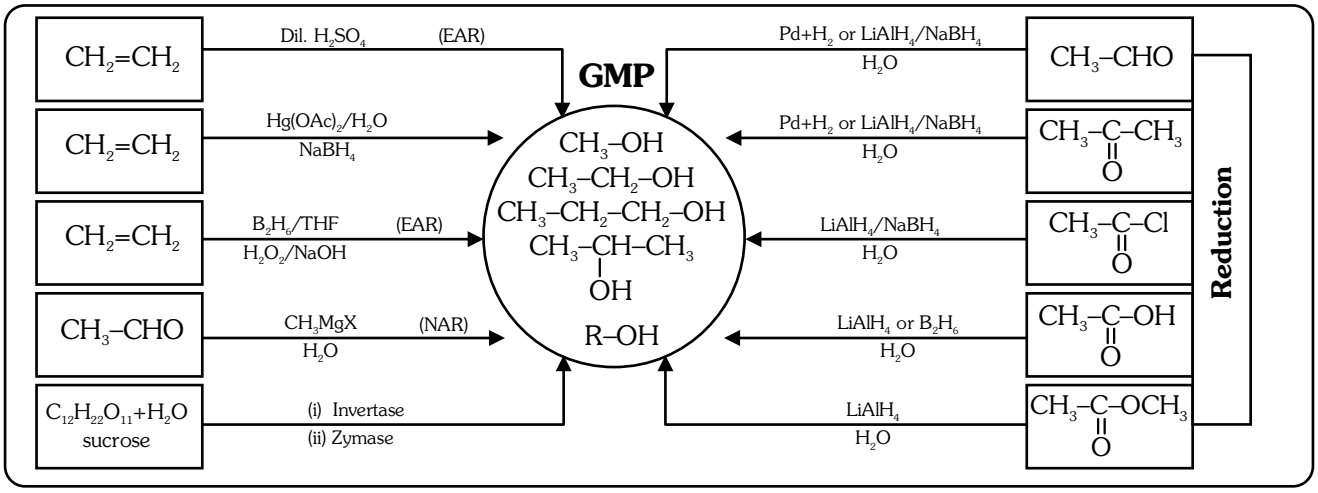
(Active H-containing compound)

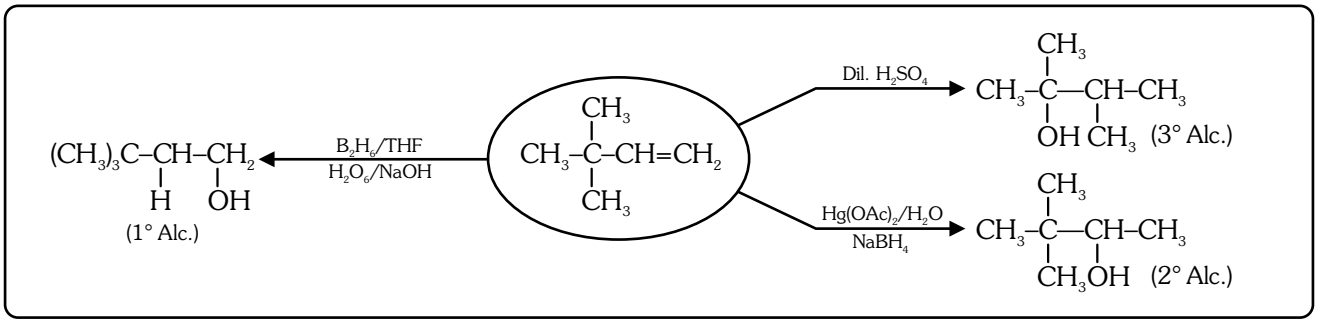


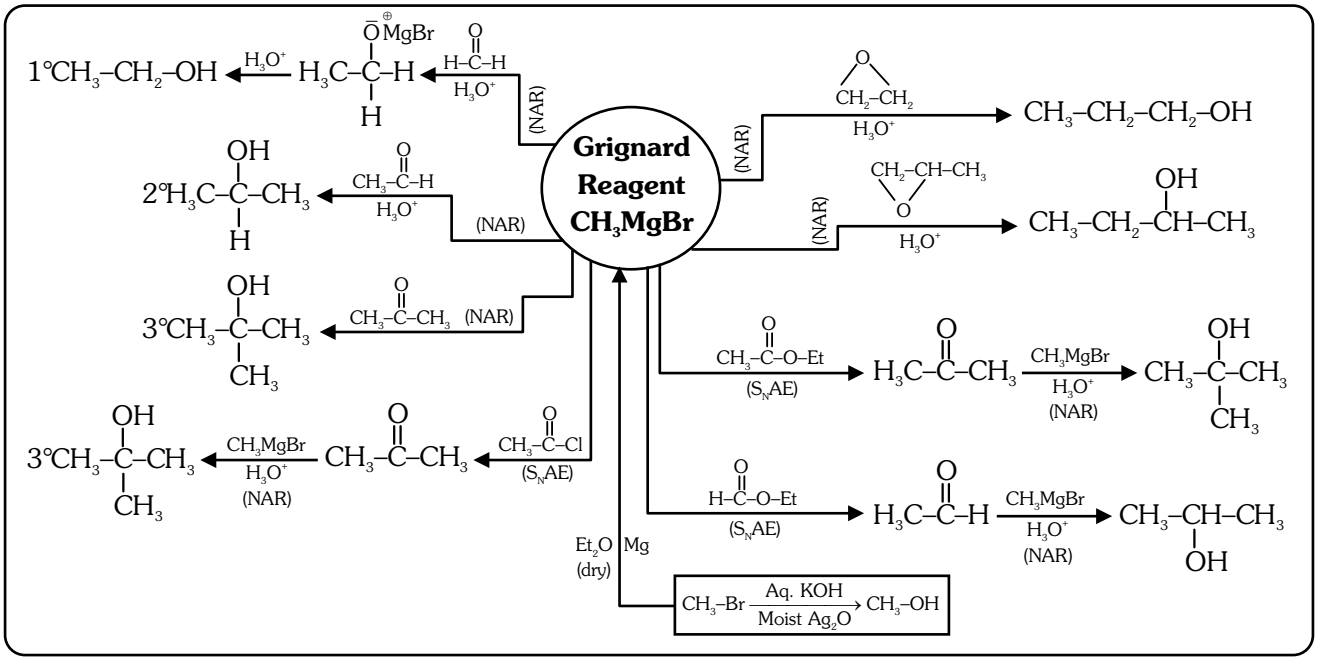
IMPORTANT NOTE

CHAPTER 08

ALCOHOL

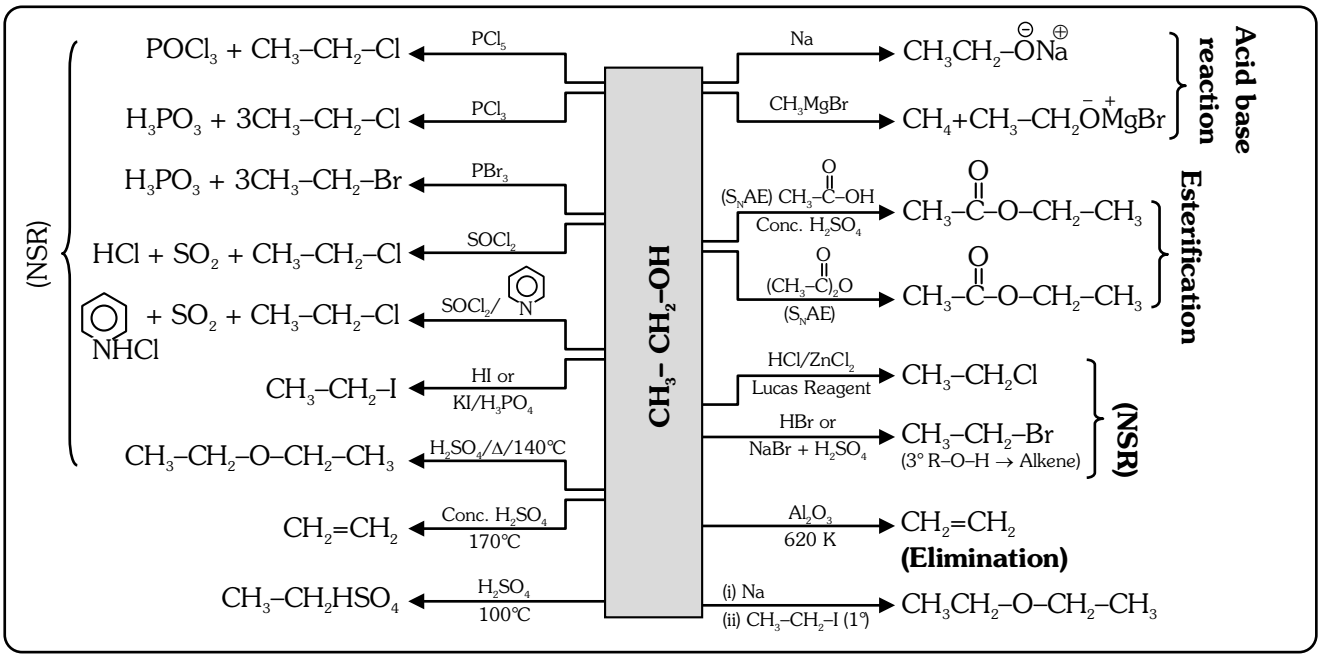






- Solubility of alcohol increase with increase in branching n < iso < neo (isomeric)
- Relative order of reactivity

  (i) 1° > 2° > 3° (O–H bond fission) (ii) 3° > 2° > 1° (C–O bond fission) (iii) 3° > 2° > 1° (Dehydration)


(NSR)
$POCl_3 + CH_3–CH_2–Cl$ ← PCl_5
$H_3PO_3 + 3CH_3–CH_2–Cl$ ← PCl_3
$H_3PO_3 + 3CH_3–CH_2–Br$ ← PBr_3
$HCl + SO_2 + CH_3–CH_2–Cl$ ← $SOCl_2$
$+ SO_2 + CH_3–CH_2–Cl$ ← $SOCl_2$/ N
NHCl
$CH_3–CH_2–I$ ← HI or KI/H_3PO_4
$CH_3–CH_2–O–CH_2–CH_3$ ← $H_2SO_4/\Delta/140°C$
$CH_2=CH_2$ ← Conc. H_2SO_4 170°C
$CH_3–CH_2HSO_4$ ← H_2SO_4 100°C
$CH_3–CH_2–OH$
Na → $CH_3CH_2–O^{\ominus}Na^{\oplus}$
CH_3MgBr → $CH_4 + CH_3–CH_2–O^{-}Mg^{+}Br$
Acid base reaction
(SNAE) $CH_3–COOH$, Conc. H_2SO_4 → $CH_3–COO–CH_2–CH_3$
$(CH_3–C)_2O$ (SNAE) → $CH_3–COO–CH_2–CH_3$
Esterification
$HCl/ZnCl_2$ Lucas Reagent → $CH_3–CH_2Cl$
HBr or $NaBr + H_2SO_4$ → $CH_3–CH_2–Br$ (3° R–O–H → Alkene)
(NSR)
Al_2O_3 620 K → $CH_2=CH_2$
(Elimination)
(i) Na (ii) $CH_3–CH_2–I$ (1°) → $CH_3CH_2–O–CH_2–CH_3$

DEHYDROGENATIONS (OXIDATION)

Reagent	$H_3C–CH_2–CH_2–CH_2OH$ 1° Alcohol	$H_3C–CH_2–CH(OH)–CH_3$ 2° Alcohol	$H_3C–C(CH_3)_2–OH$ 3° Alcohol
PCC/PDC Anhy. CrO_3	$H_3C–CH_2–CH_2–CHO$	$H_3C–CH_2–CO–CH_3$	No reaction
$K_2Cr_2O_7/H^{\oplus}$ $KMnO_4/H^{+}/\bar{O}H/\Delta$ Jones Reagent	$H_3C–CH_2–CH_2–COOH$	$H_3C–COOH + CH_3–COOH$	No reaction
Cu/300°C	$H_3C–CH_2–CH_2–CHO$	$CH_3–CH_2–CO–CH_3$	$H_3C–C(CH_3)=CH_2$
Lucas Reagent $HCl/ZnCl_2$	Cloudiness appear upon heating after 30 mins.	within five min.	Immediately

VICTOR MEYER'S TEST

P/I_2	$CH_3–CH_2–CH_2–CH_2–I$	$H_3C–CH_2–CH(CH_3)–I$	$H_3C–C(CH_3)_2–I$
$AgNO_2$	$CH_3–CH_2–CH_2–NO_2$	$H_3C–CH_2–CH(CH_3)–NO_2$	$(CH_3)_3C–NO_2$
HNO_2	$CH_3–CH_2–C(=N–OH)–NO_2$ Nitrolic acid	$H_3C–CH_2–C(CH_3)(N=O)–NO_2$	No reaction
NaOH	Red colour	Blue colour	Colourless

ETHER

GMP

$2C_2H_5–OH$
[Williamson continuous etherification]
(NSR) [S_N2]

$H_2SO_4/140°C$

$H_3C–CH_2–\bar{O}Na^+$
[Williamson synthesis] [3°(R–X)→Alkene]
(NSR) [S_N2]

$CH_3–CH_2–I$

$2C_2H_5I$

Dry Ag_2O

$H_3C–CH_2–O–CH_2–CH_3$
$H_3C–CH_2–O–CH_3$
R–O–R

Reactions

HCl
Cold

$\left[\begin{matrix}H\\|\\(C_2H_5)_2O\end{matrix}\right]^+ Cl–$

HI
(NSR)

(HI > HBr > HCl)
$CH_3–CH_2I + CH_3–CH_2–OH$

HI/Δ
excess

$CH_3–CH_2I + CH_3–CH_2–I$

PHENOL

GMP

SO_3Na

(i) NaOH
(ii) $H^\oplus$

$N_2^+Cl^-$

H_2O/Δ

COOH
OH

$NaOH + CaO/\Delta$

OH
PHENOL

(i) $O_2 + \Delta$
(ii) $H^\oplus/H_2O$
($–CH_3COCH_3$)
other product

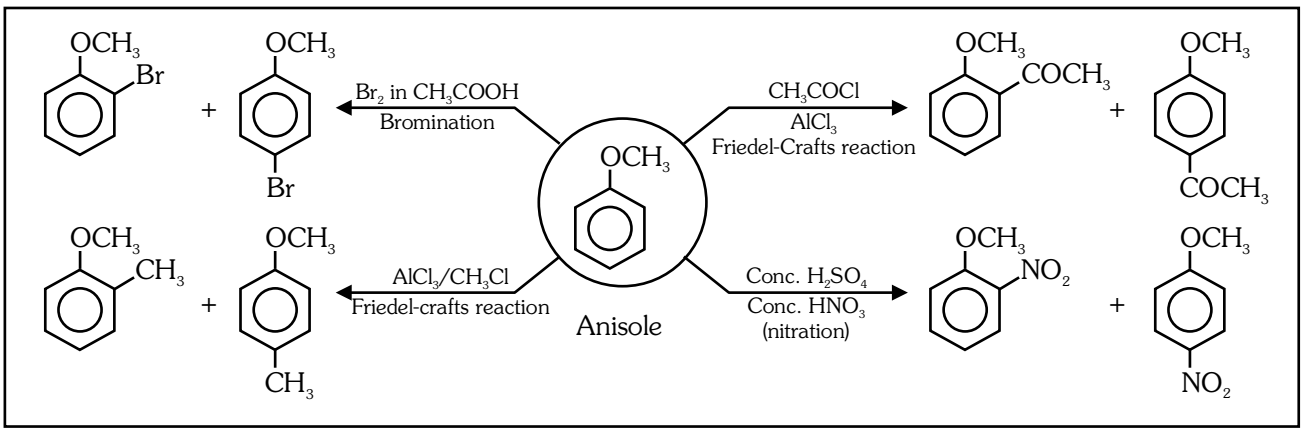
CH_3
$H_3C–\overset{|}{C}–H$

1. O_2/Air Oxidation
2. H_2O

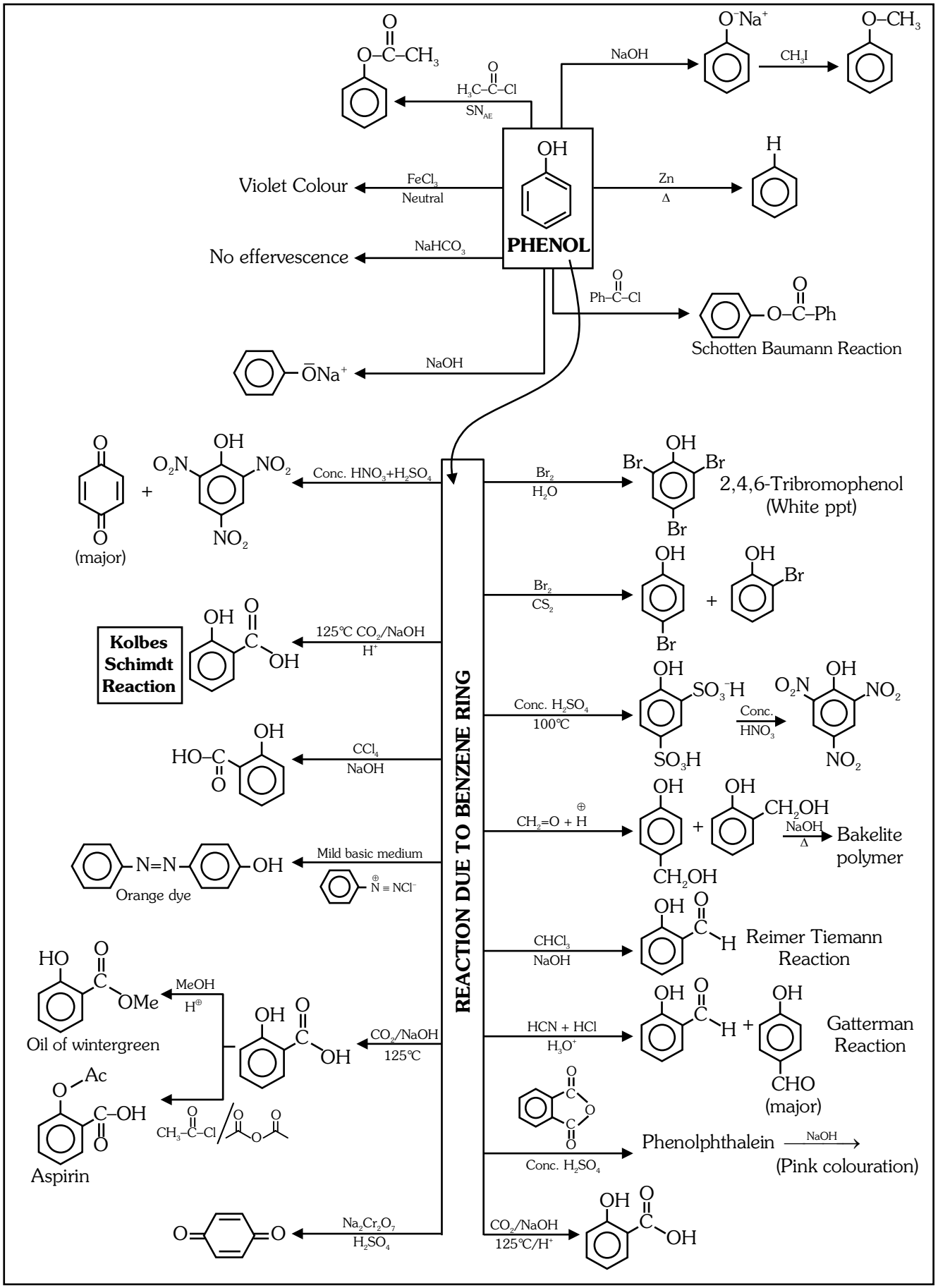
MgCl

O_2, V_2O_5
300°C

H



PHENOL


PHENOL
NaOH
CH3I
H3C–C–Cl
SNAE
Violet Colour
FeCl3
Neutral
Zn
Δ
No effervescence
NaHCO3
Ph–C–Cl
Schotten Baumann Reaction
NaOH
(major)
Conc. HNO3+H2SO4
Br2
H2O
2,4,6-Tribromophenol
(White ppt)
Br2
CS2
Kolbes
Schimdt
Reaction
125°C CO2/NaOH
H+
Conc. H2SO4
100°C
Conc.
HNO3
CCl4
NaOH
CH2=O + H
NaOH
Δ
Bakelite
polymer
Mild basic medium
Orange dye
CHCl3
NaOH
Reimer Tiemann
Reaction
MeOH
H⊕
Oil of wintergreen
CO2/NaOH
125°C
HCN + HCl
H3O+
Gatterman
Reaction
(major)
Aspirin
Phenolphthalein
NaOH
(Pink colouration)
Conc. H2SO4
Na2Cr2O7
H2SO4
CO2/NaOH
125°C/H+
REACTION DUE TO BENZENE RING

Comparision of S_N1 and S_N2

REACTIONS		S_N1	S_N2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][Nu:$^{\ominus}$]
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	3°> 2°>1°>MeX	MeX >1°>2°>3°
E	Nucleophile	Rate Independent	Needs Strong $Nu^{\ominus}$
F	Solvent	Good in protic	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Comparision of E_1 and E_2

REACTIONS		E1	E2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][B:$^{-}$]
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	3° > 2°>>>1°	3° >2° >1°
E	Base Strength	Rate Independent	Needs Strong bases
F	Solvent	Good ionizing	Polarity not important
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

Summary of S_N1, S_N2, E_1 and E_2 Reactions

RX	Mechanism	$\overset{\ominus}{Nu}/\overset{\ominus}{B}$	Solvent	Temp.
1°	S_N2	Better $Nu^{\ominus}$ Aq. KOH, $OR^{\ominus}$	Polar aprotic	Low
	E2	Strong & bulky base Alc. KOH, $(CH_3)_3CO^{\ominus}$		High
2°	S_N2	Aq. KOH	Polar aprotic	Low
	E2	$OR^{\ominus}$, $(CH_3)_3CO^{\ominus}$		High
	(S_N1)	Solvent	Polar protic	(Low)
	(E1)	Solvent		(High)
3°	S_N1	Solvent	Protic	Low
	E1	Solvent	Protic	High
	E2	$Nu^{\ominus}$/Base	—	High

	Primary (1°)	Secondary (2°)	Tertiary (3°)
Strong nucleophile	S_N2 >>E2	S_N2 + E_2 (if weak base, S_N2 favored)	E2
Weak nucleophile weak base	Mostly S_N2	Mostly S_N2/S_N1	Mostly S_N1 at low T mostly E1 at high T
Weak nucleophile strong base	Mostly E2	Mostly E2	E2

Order of reactivity of Alkyl Halide towards

$S_N1 \propto$ ● Benzylic > Allylic
● 3°>2°>1°

$S_N1 \propto$ Stability of carbocation

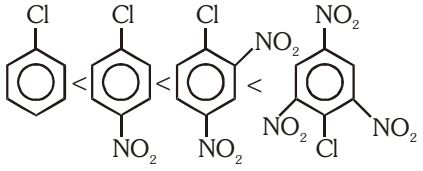
$S_N2 \propto 1° > 2° > 3°$

$$S_N2 \propto \frac{1}{\text{Steric hindrance}}$$

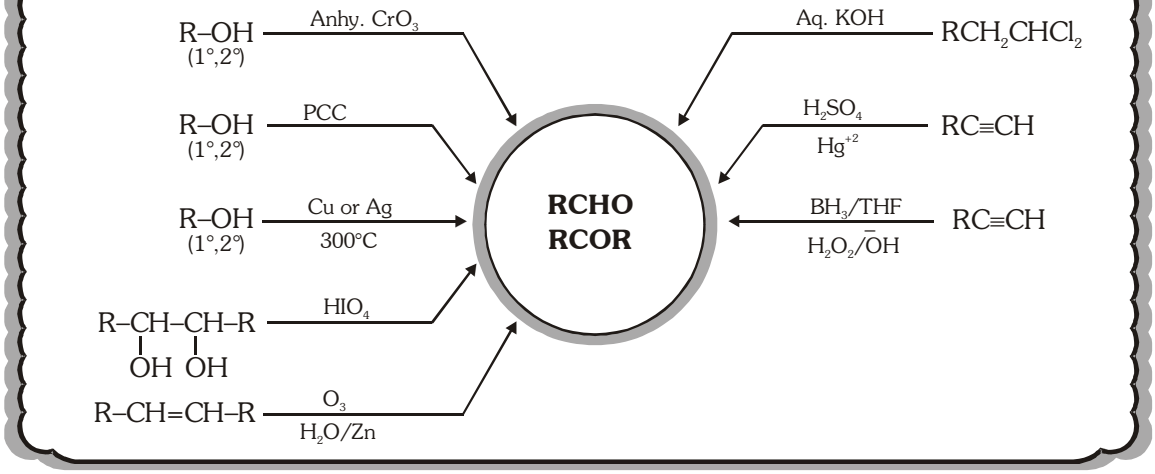
Reactivity order towards S_N1 or S_N2 and E_1 or E_2

R–I > R–Br > R–Cl > R–F

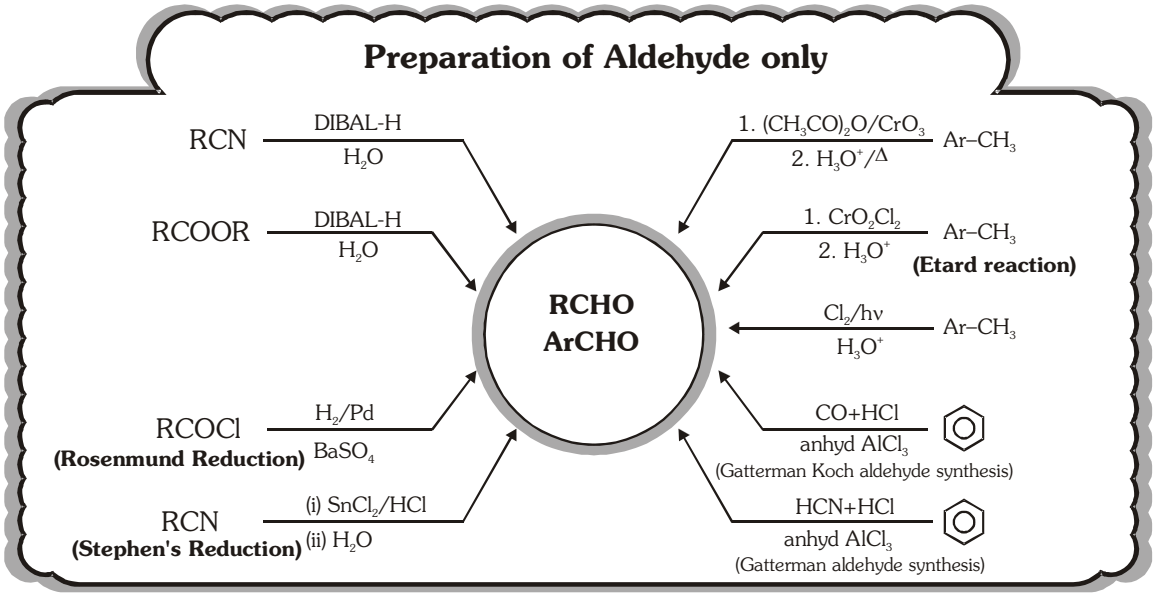
With increase in number of strong electron withrawing group at ortho and para position, reactivity of X towards aromatic nucleophilic substitution (SN^{Ar}) increases.



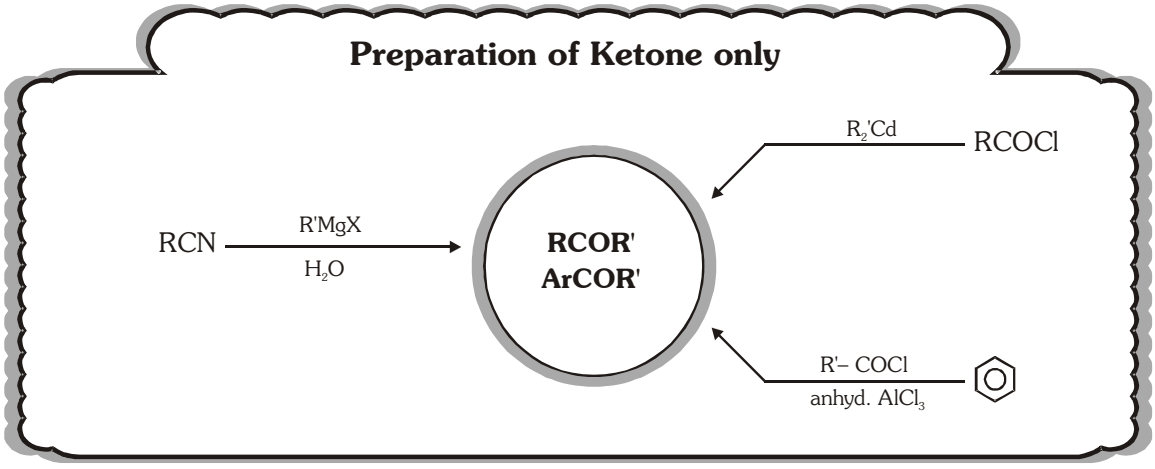
Preparation of Aldehyde & Ketone both



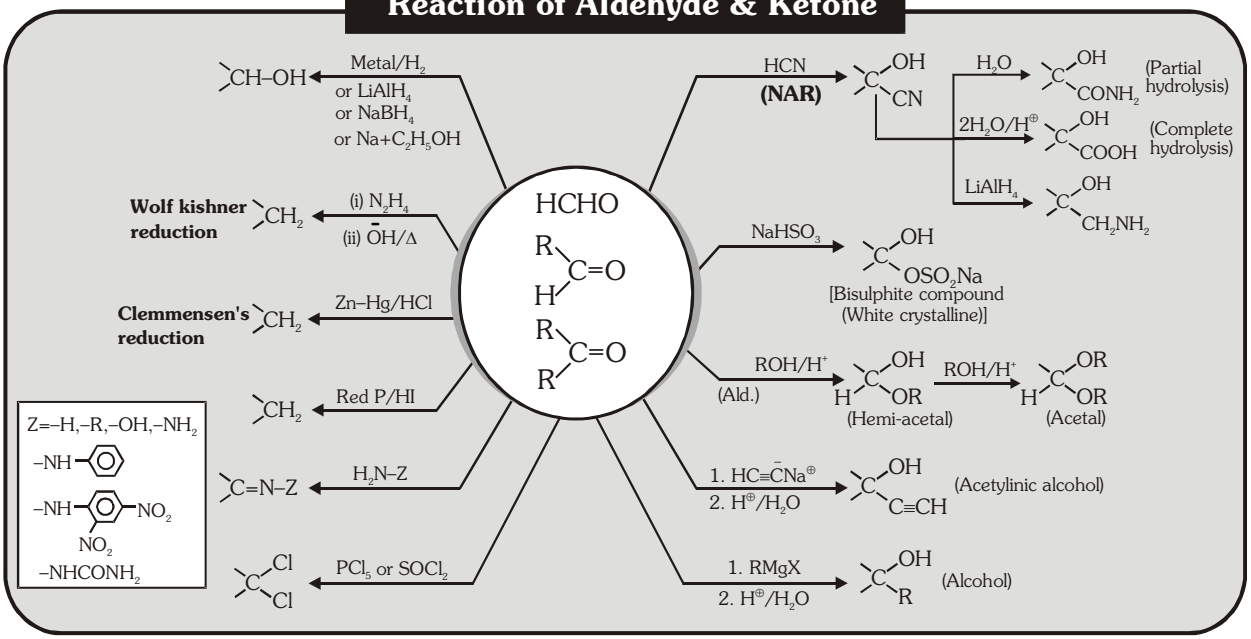
Preparation of Aldehyde only


RCN — DIBAL-H, H_2O
RCOOR — DIBAL-H, H_2O
RCOCl — H_2/Pd, $BaSO_4$ (Rosenmund Reduction)
RCN — (i) $SnCl_2/HCl$, (ii) H_2O (Stephen's Reduction)
1. $(CH_3CO)_2O/CrO_3$, 2. H_3O^+/Δ — $Ar–CH_3$
1. CrO_2Cl_2, 2. H_3O^+ — $Ar–CH_3$ (Etard reaction)
$Cl_2/h\nu$, H_3O^+ — $Ar–CH_3$
CO+HCl, anhyd $AlCl_3$ (Gatterman Koch aldehyde synthesis)
HCN+HCl, anhyd $AlCl_3$ (Gatterman aldehyde synthesis)
RCHO
ArCHO

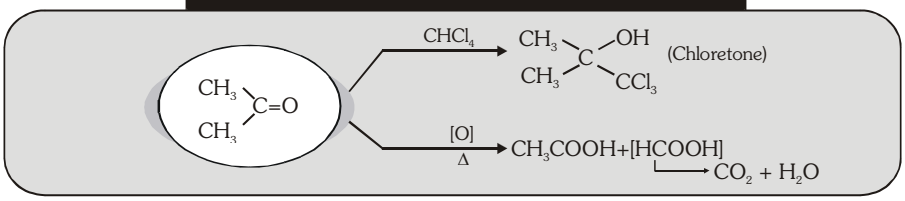
Preparation of Ketone only



Reaction of Aldehyde & Ketone



Reaction of only Ketone



Aldol Reaction (Aldehyde or ketone with αH)

(i) $2CH_3CHO \xrightleftharpoons{\text{dil. NaOH}} CH_3–\underset{\underset{\text{Aldol}}{|}}{\underset{OH}{CH}}–CH_2–CHO \xrightarrow[-H_2O]{\Delta} CH_3–CH=CH–CHO$ (Aldol condensation product)

(ii) $2CH_3COCH_3 \xrightleftharpoons{Ba(OH)_2} CH_3–\underset{\underset{\text{Ketol}}{|}}{\underset{OH}{C}}–CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} CH_3–\underset{CH_3}{\underset{|}{C}}=CH–COCH_3$ (Aldol condensation product)

Cannizzaro reaction (Aldehyde with no αH)

$2HCHO \xrightarrow[\Delta]{\text{conc. NaOH}} CH_3OH + HCOO^-Na^+$

TESTS

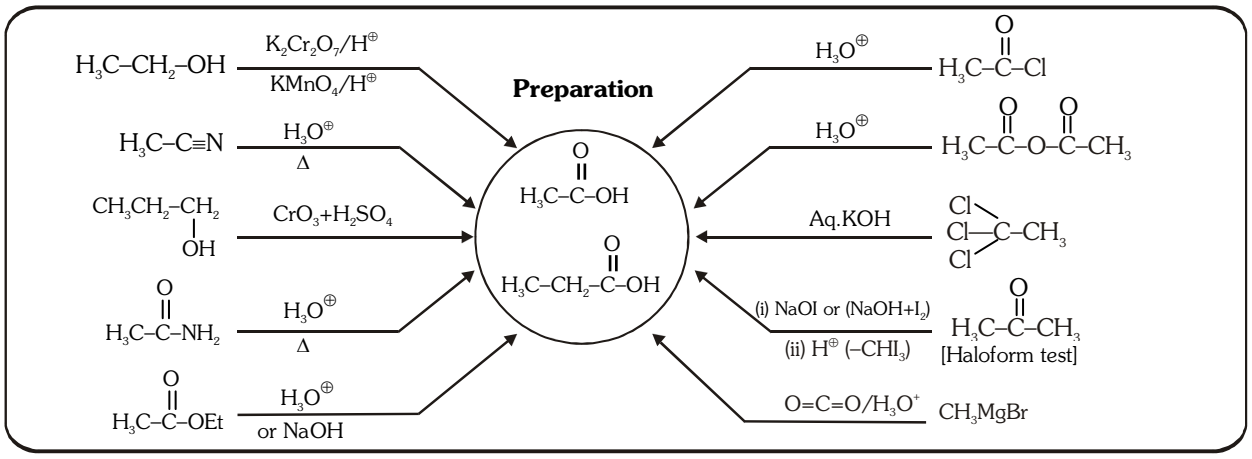
Tollen's test
$RCHO + 2[Ag(NH_3)_2]^+ + 3\ ^-OH \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$
(Given by Aliphatic and aromatic aldehyde)

Fehling's test
$RCHO + 2Cu^{+2} + 5\ ^-OH \longrightarrow RCOO^- + Cu_2O + 3H_2O$
(Given by Aliphatic aldehyde) (Red-Brown ppt.)

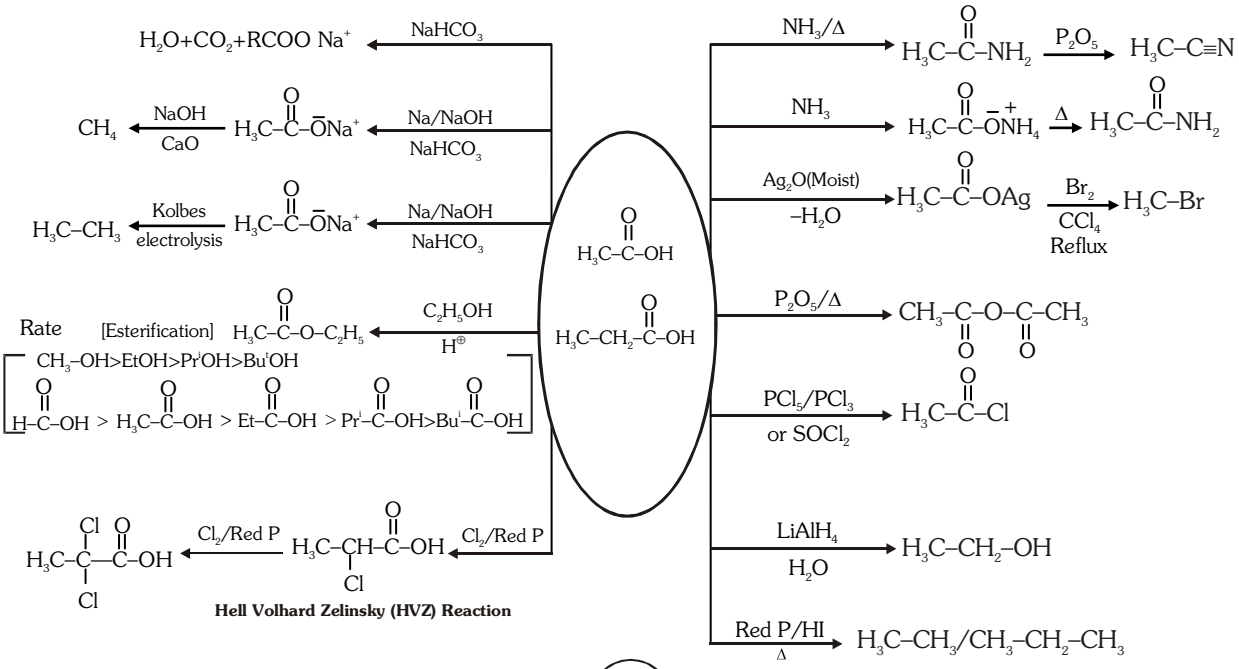
IMPORTANT NOTE

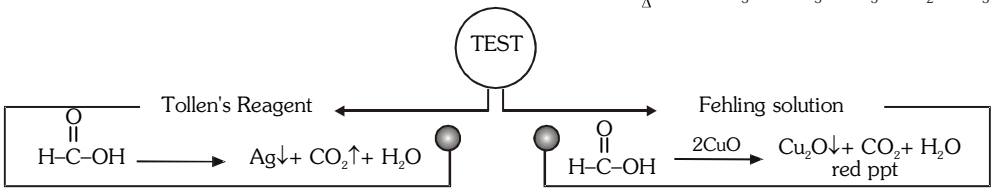
CHAPTER 9

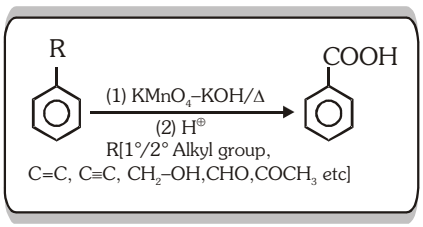
CARBOXYLIC ACID

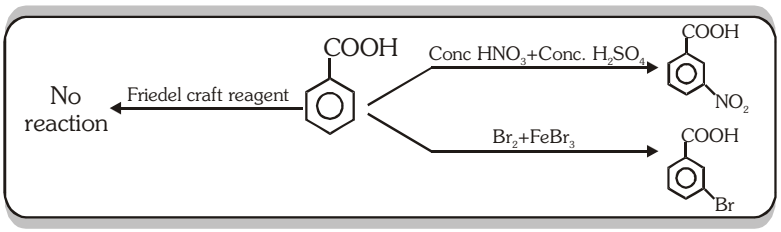


Reactions







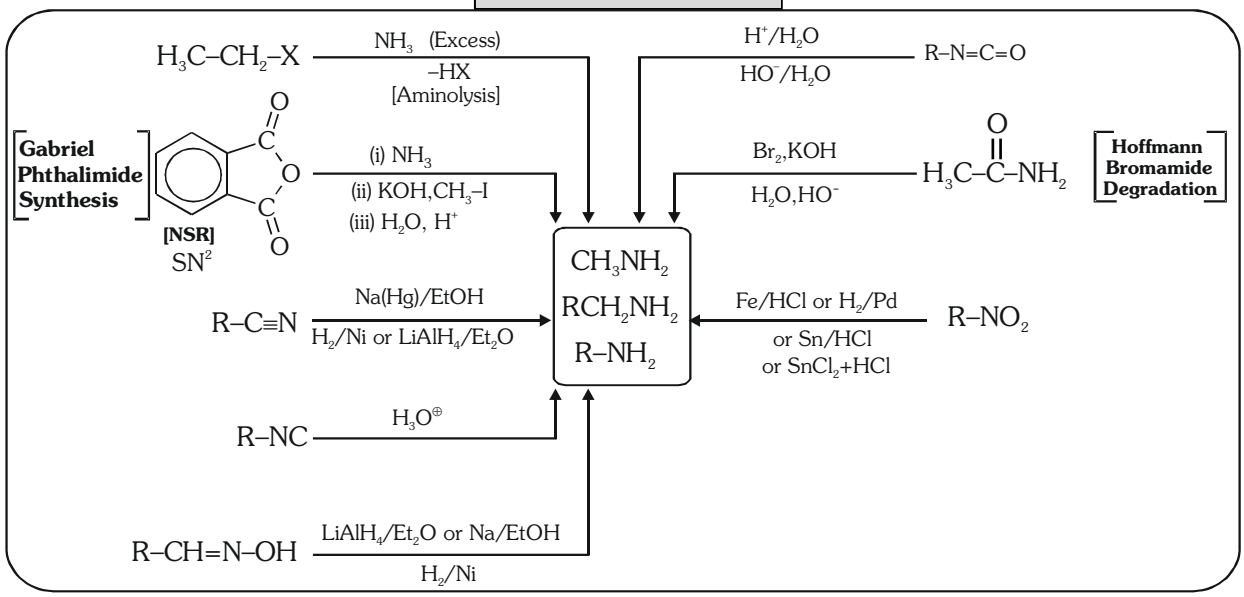


IMPORTANT NOTE

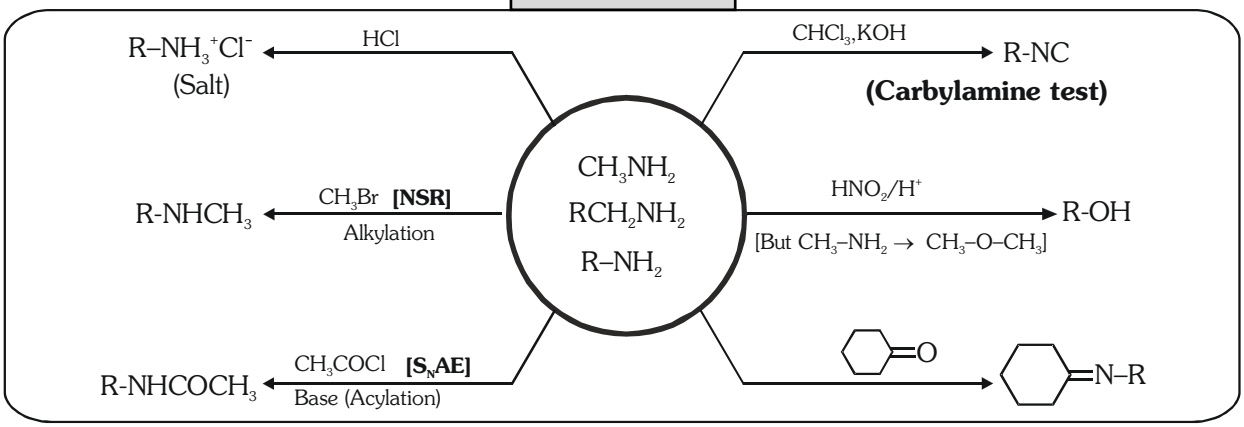
CHAPTER 10

AMINES

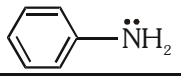
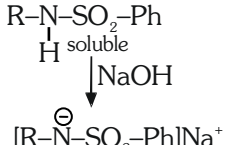
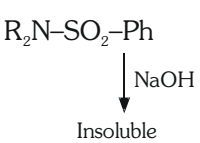
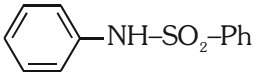
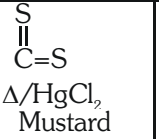
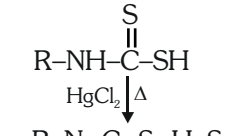
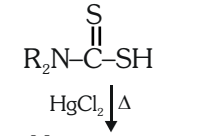
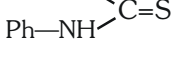
PREPARATION



REACTION

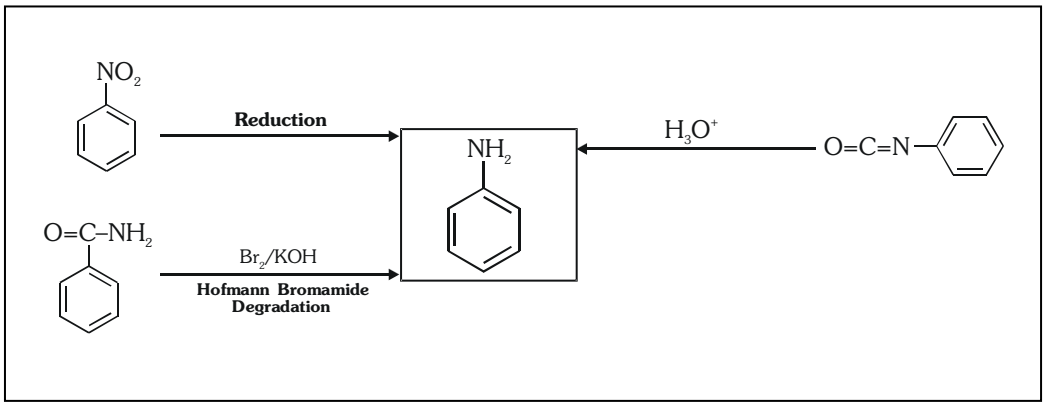


TEST

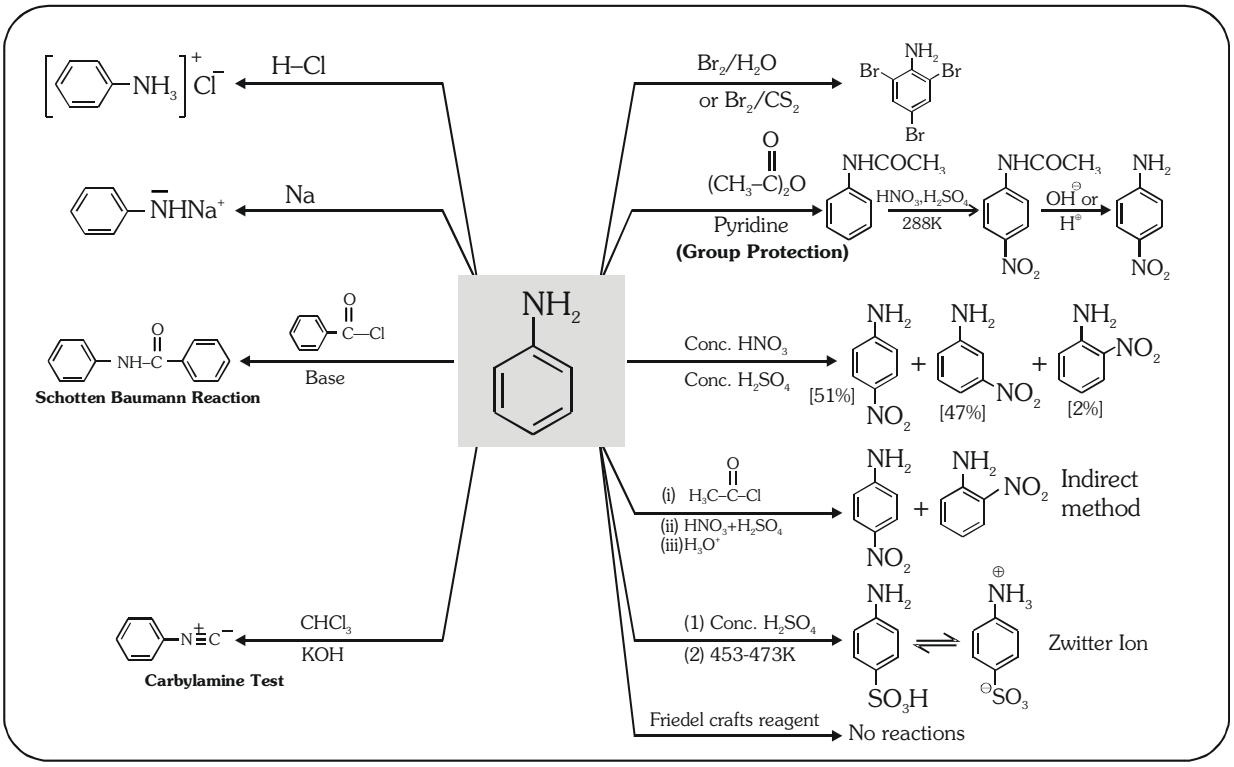
Reagent	R–$\ddot{N}H_2$(1°)	$R_2\ddot{N}H$(2°)	$R_3\ddot{N}$(3°)	
$Ph–SO_2Cl$ (Hinsberg reagent)			No reaction	 Soluble in base
 Mustard oil test			No reaction	

ANILINE

PREPARATION

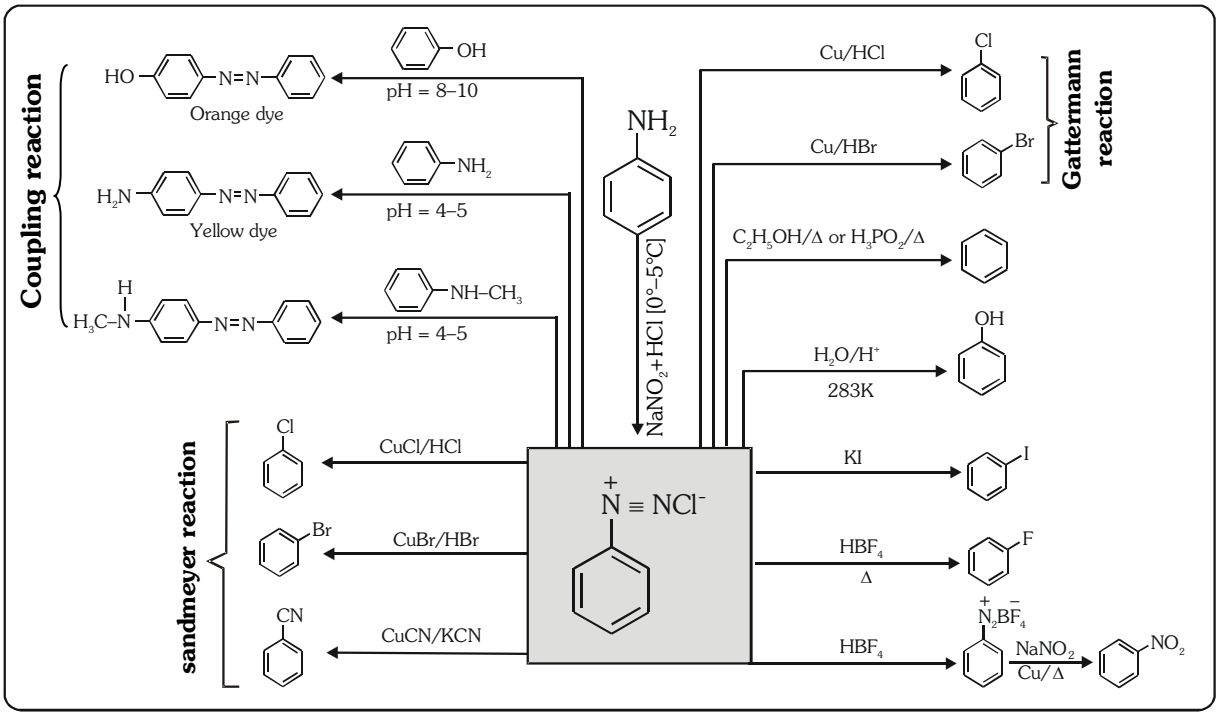


REACTION



BENZENE DIAZONIUM CHLORIDE

REACTION



FrSR	Free Radical Substitution reaction
ESR	Electrophilic Substitution reaction
NSR	Nucleophilic Substitution reaction
S_NAE	Substitution Nucleophilic (addition elimination)
FrAR	Free radical addition reaction
NAR	Nucleophilic addition reaction
EAR	Electrophilic addition reaction
FrER	Free Radical Elimination reaction

IMPORTANT NOTE

CHAPTER 11

Nutshell review & preview of ORGANIC REAGENTS

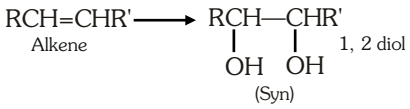
1. Alcoholic KOH

R—X → Alkene (Elimination)

2. Aqueous KOH/NaOH

R—X → ROH

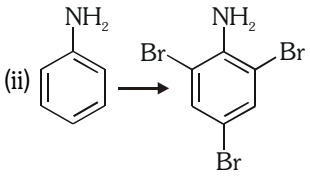
3. Baeyer's Reagent (Alkaline cold dilute $KMnO_4$)



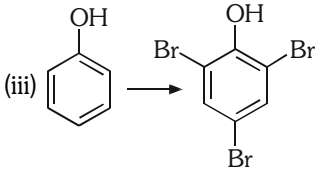
(used to detect unsaturation)

4. Bromine water

(i) used to detect unsaturation;



2,4,6-tribromoaniline (White PPT)



2,4,6-tribromophenol (White PPT)

5. Benedict's solution

Used to detect aldehyde group, RCHO→ RCO_2^-

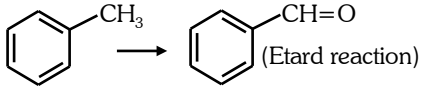
[ketone gives –ve test]

6. Cu_2Cl_2 + NH_4OH

Used to Detect Terminal Alkyne

Red Precipitate observed

7. CrO_2Cl_2



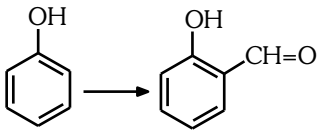
8. CrO_3

(i) $RCH_2OH \rightarrow$ RCHO,

(ii) $R_2CHOH \rightarrow R_2C=O$

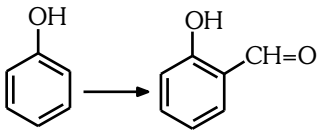
(iii) $R_3COH \rightarrow$ no reaction

9. CO + HCl + $AlCl_3$



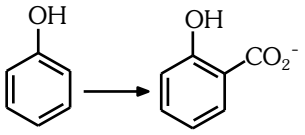
(Gatterman koch reaction)

10. HCN + HCl + $AlCl_3$

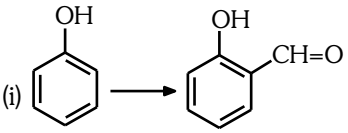


(Gatterman Aldehyde Synthesis)

11. $CCl_4 + OH^-$ (Reimer Tiemann)



12. $CHCl_3$ + KOH

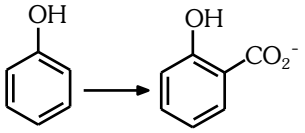


(Reimer Tiemann reaction)

(ii) $RNH_2 \rightarrow$ RNC (Carbylamine reaction)

(used to detect 1° Amine) (Isocyanide test)

13. $CO_2 + OH^-$ (high temp. + Pressure)

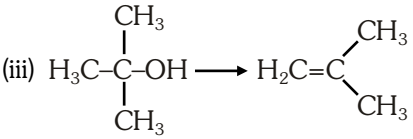


(Kolbe's reaction)

14. Cu/Δ

(i) $RCH_2OH \rightarrow$ RCHO,

(ii) $R_2CHOH \rightarrow R_2C=O$



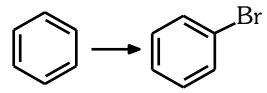
15. 2,4 – D.N.P.

used to detect carbonyl group (orange ppt observed)

16. DMSO

Polar aprotic solvent: favour S_N^2 mechanism

17. Fe or $FeBr_3$ + Br_2



18. Fehling solution

used to identify – CH=O group.

PhCHO gives –ve test

Observation: red ppt of Cu_2O formed

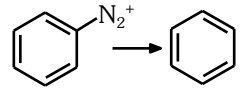
19. Grignard Reagent

Follows (i) Acid base reaction (ii) NAR (iii) NSR

20. H_2(Pd/$CaCO_3$) Quinoline (Lindlar catalyst)

R—C≡C—R → R—CH=CH—R (cis)

21. H_3PO_2



22. H_3PO_4/Δ

H_3PO_4 ⇒ Same as H_2SO_4/Δ (Alcohol → Alkene)

23. H_2SO_4/Δ

$RCH(OH)-CH_3 \longrightarrow \underset{\text{(Alkene)}}{RCH=CH_2}$

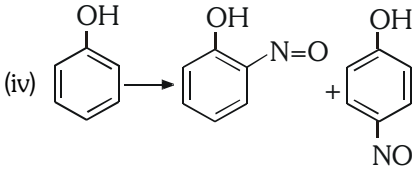
Saytzeff product; C^+ mechanism;

24. HNO_2 ($NaNO_2$ + HCl)

(i) $RNH_2 \rightarrow$ R—OH;

(ii) $PhNH_2 \rightarrow PhN_2^+$ (0 – 5°C)

(iii) $PhNH_2 \rightarrow$ PhOH (high temperature)

(iv) 

25. HIO_4 (Periodic acid)

$RCH(OH)-CH(OH)-R' \longrightarrow RCH=O + R'CH=O$

Oxidative cleavage of diol

26. H_2(Ni) can reduce

(i) $R-\underset{\underset{O}{\|}}{C}-R \longrightarrow R_2CHOH$

(ii) $R-\underset{\underset{O}{\|}}{C}-H \longrightarrow RCH_2OH$

(iii) $RCN \rightarrow RCH_2NH_2$

$-C\equiv C- \rightarrow -CH_2-CH_2-$

$-HC=CH- \rightarrow -CH_2—CH_2-$

27. H_2–Pd/$BaSO_4$ or Quinoline

$R-\underset{\underset{O}{\|}}{C}-Cl \longrightarrow RCH=O$ (Rosenmund reduction)

28. Jones Reagent (CrO_3+dil. H_2SO_4+ acetone)

(i) $RCH_2OH \rightarrow$ R–COOH; (ii) $R_2CHOH \rightarrow R_2C=O$

29. $K_2Cr_2O_7/H^+$

(i) $RCH_2OH \rightarrow RCO_2H$; (ii) $R_2CHOH \rightarrow R_2C=O$

30. $NaHCO_3$

$RCO_2H \xrightarrow{NaH\overset{14}{C}O_3} RCO_2^-Na^+ + \overset{14}{C}O_2\uparrow$

31. $NaHSO_3$

$R-\underset{\underset{O}{\|}}{C}-R \longrightarrow \underset{R}{\overset{R}{>}}C\underset{SO_3^-Na^+}{\overset{OH}{<}}$

[White crystals, soluble in water used to separate carbonyl from noncarbonyl compound]

32. NaOH(aq)

(i) R—X → R—OH

(ii) $R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[(H_2O)]{NaOH} R-\underset{\underset{O}{\|}}{C}-O^- + R'OH$

Basic hydrolysis of ester

(iii) $HCHO \xrightarrow{OH^-} HCO_2^- + CH_3OH$

(Cannizzaro reactiion)

(iv) $H_3C-CH=O \xrightarrow[2.\Delta]{1.OH^-} H_3C-CH=CH-CH=O$

(Aldol condensation)

33. NaOR

Strong base :

(i) $RCH(X)-CH_2-R \longrightarrow RCH=CH-R$

(Saytzeff Product : E_2 elimination)

34. NaOH + X_2 or NaOX

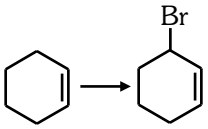
(i) $RC(=O)-CH_3 \xrightarrow{-CHI_3} RCO_2^-$ (Haloform reaction)

(ii) $R-\underset{\underset{O}{\|}}{C}-NH_2 \longrightarrow RNH_2$ **(Hoffman Degradation or Bromamide)**

35. NaOH + CaO (Sodalime)

$RCO_2H \rightarrow RH$

36. NBS (Allylic, benzylic substitution)

(i)  ; (ii) $PhCH_3 \rightarrow PhCH_2–Br$

37. $NaNO_2$ + HCl

$RNH_2 \rightarrow R—OH$

38. $NaNH_2$

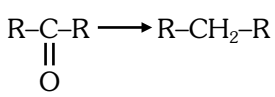
Non-terminal Alkyne → Terminal Alkyne

(2–Butyne → 1–butyne)

39. Na/EtOH

Reduce all π-bonds except c/c double & triple bond

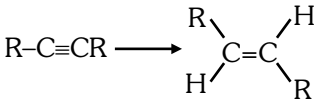
40. Zn(Hg) + HCl [Clemmensen's reduction]



41. $NH_2–NH_2/OH^-$ [Wolf Kishner reduction]

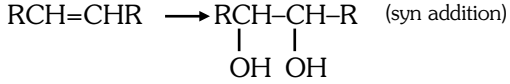
$R–CO–R \rightarrow R–CH_2–R$

42. Na in Liq. NH_3 [Birch reduction]

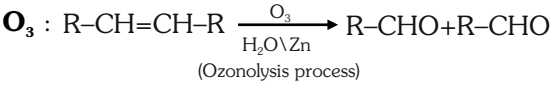


(trans alkene)

43. OsO_4 + H_2O (Hydroxylation)



(syn addition)

44. O_3 : 

(Ozonolysis process)

45. Oxirane (Cyclic ether) followed by H^+

$RMgX \rightarrow RCH_2—CH_2—OH$

46. PCC

(i) $RCH_2OH \rightarrow RCHO$

(ii) $R_2CHOH \rightarrow R_2C=O$

(iii) $R_3COH \rightarrow$ no reaction

(Mild oxidizing reagent)

47. Red(P) + Br_2

(i) $CH_3CO_2H \rightarrow$ (HVZ reaction)

(ii) $ROH \rightarrow R—Br$

48. Red(P) + HI

$CH_3CO_2H \rightarrow CH_3—CH_3$

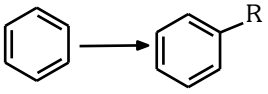
$CH_3CH=O \rightarrow CH_3—CH_3$

$CH_3CH_2OH \rightarrow CH_3—CH_3$

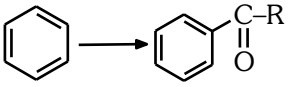
(strong reducing agent can reduce any oxygen or halogen containing compound to alkane)

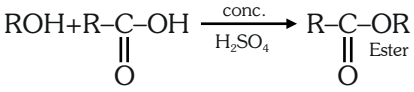
$R–X \rightarrow R–H$

49. RCl+$AlCl_3$ [Friedel craft alkylation]



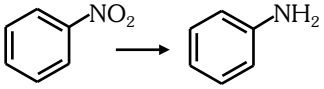
50. RCOCl + $AlCl_3$ [Friedel craft acylation]



51. 

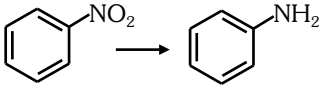
(Esterification reaction)

52. $SnCl_2$ + HCl

(i) 

(ii) $RCN \rightarrow RCH=O$ [Stephen reduction]

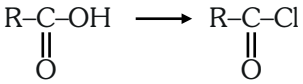
53. Sn + HCl

(i) 

(ii) $RCN \rightarrow R–CH_2NH_2$

54. AgOH/moist Ag_2O; $R_4\overset{+}{N}\bar{X} \rightarrow R_4\overset{+}{N}\bar{O}H$

55. $SOCl_2$



$R–OH \rightarrow R–Cl$

56. Tollen's Test

(i) Terminal alkyne gives

(ii) Aldehyde Group gives

(iii) Ketone group not give

(iv) α-hydroxy ketone gives

(v) HCOOH gives

(vi) Hemi acetal gives

(vii) PhNH–OH gives

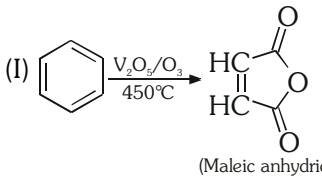
57. Benzene sulphonyl chloride (Hinsberg reagent)

It is used to test and distinguish 1°, 2° and 3° amines.

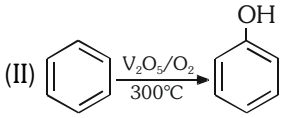
58. Tetra ethyl lead (TEL)

Used as antiknocking compound

59. V_2O_5

(I) 

(Maleic anhydride)

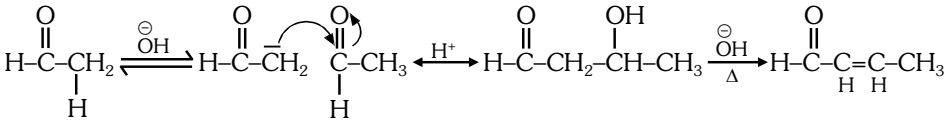
(II) 

IMPORTANT NOTE

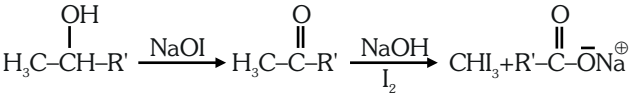
CHAPTER 12

Nutshell review & preview of ORGANIC NAME REACTIONS

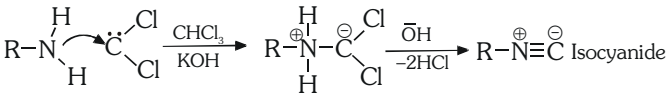
- **Aldol Condensation**



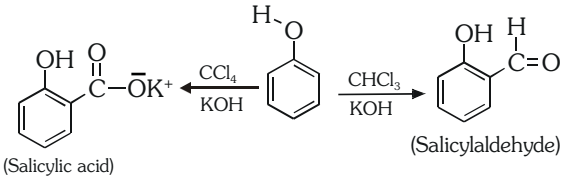
- **Haloform Reaction**



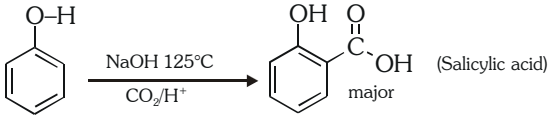
- **Carbylamine Test**



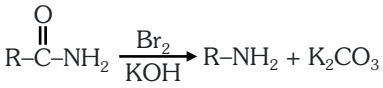
- **Reimer Tiemman Rn**



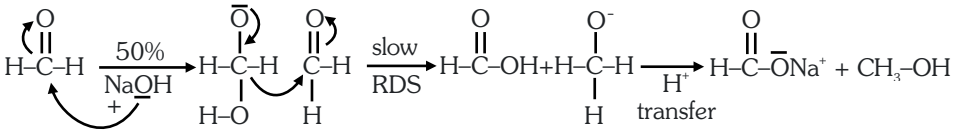
- **Kolbe's Schimdt Rn**



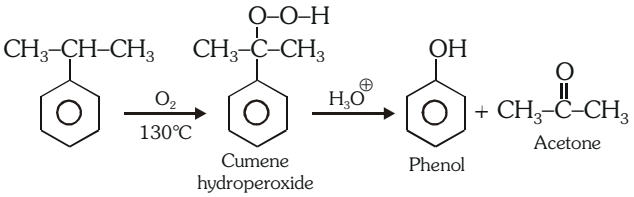
- **Hoffmann Bromamide Degradation**



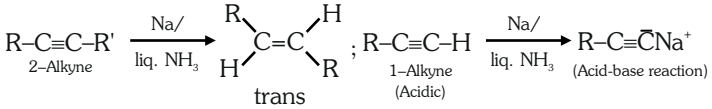
- **Cannizzaro reaction**



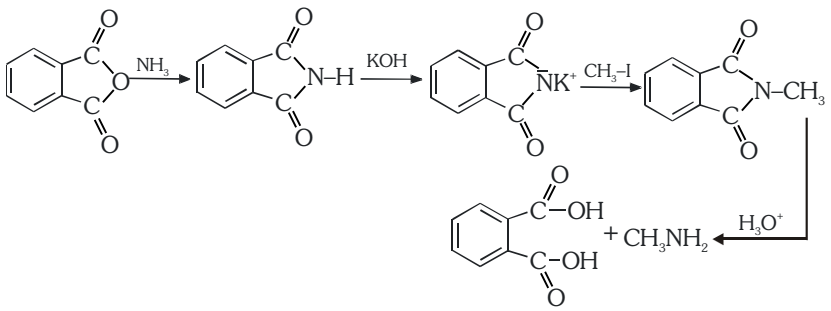
- **Cumene**



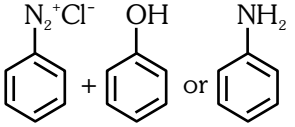
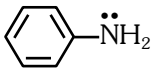
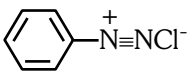
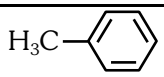
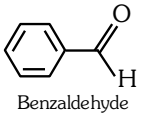
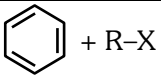
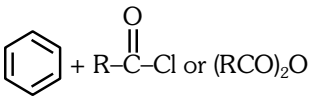
- **Birch Reduction**



- **Gabriel phthalimide Synthesis**



NAME REACTIONS

Name	Reactants	Reagents	Product
Clemmensen Reduction	Aldehyde & Ketone	Zn-Hg/conc. HCl	Alkane
Coupling Reaction		Mild basic medium for phenol, Mild acidic medium for aniline	Azo Dye (Detection of OH or NH_2 gp)
Diazotization		$NaNO_2$ + HCl (or HNO_2) 0° – 5°C	
Etard reaction		CrO_2Cl_2/CS_2	 Benzaldehyde
Fittig Reaction	Halo benzene	Na/Dry ether	Diphenyl
Friedel Craft alkylation		Anhydrous $AlCl_3$	Alkyl Benzene
Friedel Craft acylation		Anhydrous $AlCl_3$	Acyl Benzene
Gattermann aldehyde synthesis	C_6H_6	HCN+ HCl /$ZnCl_2/H_3O^+$	Benzaldehyde
Gattermann-Koch reaction	C_6H_6 + (CO + HCl)	anhy $AlCl_3$	Benzaldehyde
Hell-Volhard-Zelinsky reaction	carboxylic acid having α-hydrogen atom	Br_2 / red P	α-halogenated carboxylic acid
Hoffmann mustard oil reaction	primary aliphatic amine + CS_2	$HgCl_2/\Delta$	R—N=C=S +HgS (black)
Kolbe electrolytic reaction	alkali metal salt of carboxylic acid	electrolysis	alkane, alkene and alkyne
Mendius reaction	alkyl or aryl cyanide	Na/C_2H_5OH	primary amine
Rosenmund reduction	acid chloride	H_2, $Pd/BaSO_4$ boiling xylene	aldehyde
Sabatier-Senderens reaction	Unsaturated hydrocarbon	Raney Ni/H_2, 200—300°C	Alkane
Sandmeyer reaction	$C_6H_5\overset{+}{N}_2\,Cl^-$	CuCl/HCl or CuBr/HBr or CuCN/KCN, heat	Halo or cyanobenzene
Gattermann Reaction	$C_6H_5N_2^+Cl^-$	Cu/HX(HBr/HCl)	Halobenzene
Schotten-Baumann reaction	(phenol or aniline or alcohol)	NaOH + C_6H_5COCl	benzolytated product
Stephen reaction	alkyl cyanide	(i) $SnCl_2$/HCl (ii) H_2O	Aldehyde
Williamson synthesis	alkyl halide	sodium alkoxide or sodium phenoxide	Ether
Wurtz-Fittig reaction	alkyl halide + aryl halide	Na/dry ether	alkyl benzene

IMPORTANT NOTE

CHAPTER 13

CARBOHYDRATES

- Carbohydrates are defined as optically active polyhydroxy aldehydes or ketones or the compound which produce such units on hydrolysis.
- **Monosaccharide ($C_nH_{2n}O_n$) :** single unit, can't be hydrolysed : Glucose and fructose.
- **Oligosaccharides** gives two to ten monosaccharides on hydrolysis.
- **Disaccharides** (by glycosydic linkage)

  * Sucrose $\xrightarrow{H_3O^+}$ α-D. Glucose + β-D Fructose;

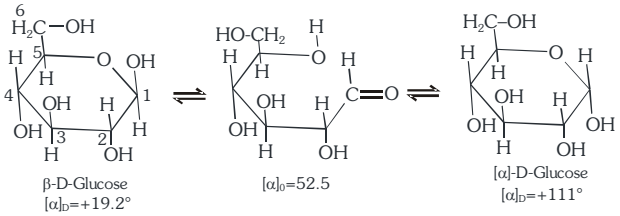
  * Maltose $\xrightarrow{H_3O^+}$ 2 α–D. Glucose unit

  * Lactose $\xrightarrow{H_3O^+}$ β-D. Glucose + β-D Galactose
- **Polysaccharide :** Contain more than ten monosaccharide units

  $(C_6H_{10}O_5)_n$: Starch & cellulose.

Test	Reducing Sugar	Non Reducing Sugar
Tollen's Reagent	+ve test	–ve test
Fehling Reagent	+ve test	–ve test
Benedict Test	+ve test	–ve test
Mutarotation	Yes	No
Example	Glucose Fructose Mannose Galactose Maltose lactose	Sucrose Polysaccharide Starch cellulose

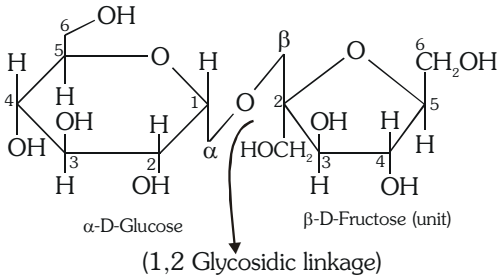
- **Mutarotation:** When either form of D-glucose is placed in aq. solution it slowly form the other via open chain aldehyde and gradual change in specific rotation until specific rotation (± 52.5°) is reached.



- **Anomer :** Differ in configuration at 1st carbon due to hemi (acetal or ketal) ring formation. The new-asymmetric carbon is referred to as Anomeric carbon.
- **Epimer :** Diastereomer's which differ in conformation at any one chiral carbon

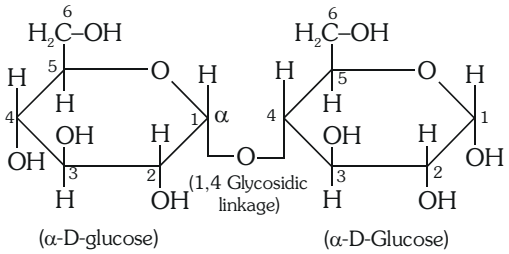
  eg. D-Glucose & D-mannose = C-2 epimer

  D-Glucose & D-Galactose = C-4 epimer
- **Sucrose :**

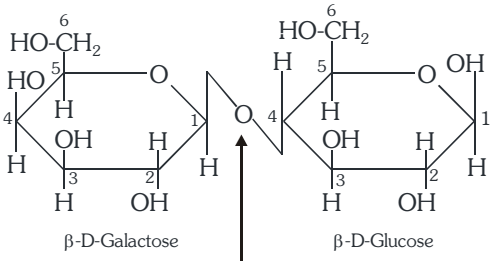


(1,2 Glycosidic linkage)

- **Maltose :**

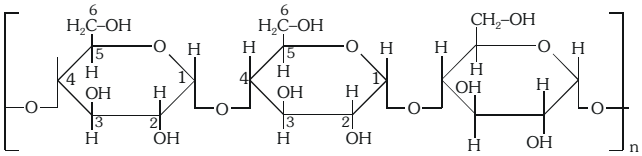


- **Lactose :**



(1,4 Glycosidic linkage)

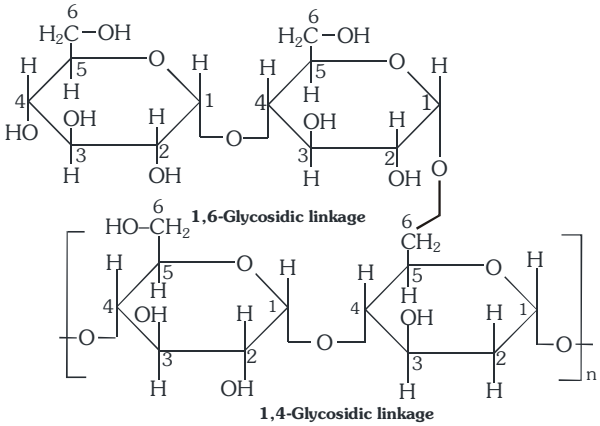
- **Starch :** (Amylose & Amylopectin)
- **Amylose :** (Straight Chain) :



(α-1,4 Glycosidic linkage)

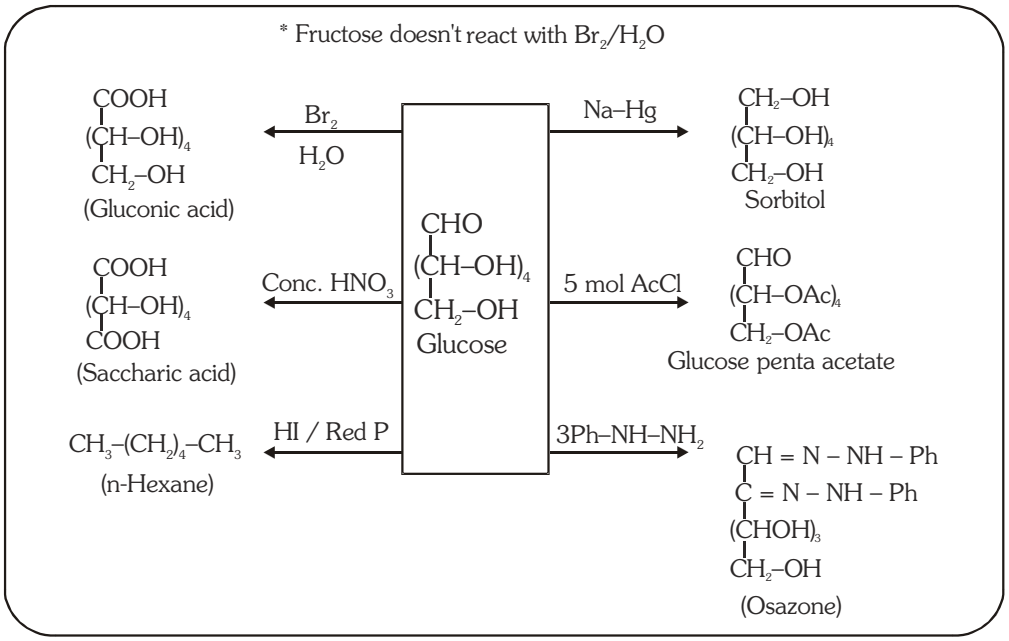
(i) Soluble in H_2O & gives blue colour with I_2

- **Amylopectin (Branch chain) :**



- Starch is polymer of α-D-Glucose
- Cellulose is polymer of β-D-Glucose

Reaction of Glucose (open chain structure)


* Fructose doesn't react with Br2/H2O
COOH (CH–OH)4 CH2–OH (Gluconic acid)
Br2 H2O
Na–Hg
CH2–OH (CH–OH)4 CH2–OH Sorbitol
CHO (CH–OH)4 CH2–OH Glucose
COOH (CH–OH)4 COOH (Saccharic acid)
Conc. HNO3
5 mol AcCl
CHO (CH–OAc)4 CH2–OAc Glucose penta acetate
CH3–(CH2)4–CH3 (n-Hexane)
HI / Red P
3Ph–NH–NH2
CH = N – NH – Ph C = N – NH – Ph (CHOH)3 CH2–OH (Osazone)

IMPORTANT NOTE